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THE  
LONDON, EDINBURGH, AND DUBLIN  
**PHILOSOPHICAL MAGAZINE**  
AND  
**JOURNAL OF SCIENCE.**

CONDUCTED BY

SIR OLIVER JOSEPH LODGE, D.Sc., LL.D., F.R.S.  
SIR JOSEPH JOHN THOMSON, O.M., M.A., Sc.D., LL.D., F.R.S.  
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RICHARD TAUNTON FRANCIS, F.R.S.E.

AND

WILLIAM FRANCIS, F.L.S.

---

"Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster  
vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit. lib. i. cap. 1.* Not.

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VOL. I.—SEVENTH SERIES.

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“Meditationis est perscrutari occulta ; contemplationis est admirari  
perspicua . . . . Admiratio generat quaestionem, quaestio investigationem,  
investigatio inventionem.”—*Hugo de S. Victore.*

—“Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condât,  
Quid toties diros cogat flagrare cometas,  
Quid pariat nubes, veniant cur fulmina coelo,  
Quo micet igne Iris, superos quis conciat orbes  
Tam vario motu.”

*J. B. Pinelli ad Mazonium.*



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[SEVENTH SERIES.]

JANUARY 1926.

I. *On the  $\delta$ -Rays produced by  $\alpha$ -Particles in Different Gases.*  
By J. CHADWICK, *Ph.D.*, *Fellow of Gonville and Caius College*, and K. G. EMELÉUS, *B.A.*, *St. John's College, Cambridge*.\*.

[Plates I. & II.]

§ 1. **W**HEN a metal plate is struck by  $\alpha$ -particles an electronic radiation is emitted, which is often called the  $\delta$ -radiation. It has been shown by Wertenstein†, Bumstead‡, and others, using polonium as the source of  $\alpha$ -particles, that  $\delta$ -rays of low velocity, corresponding to a potential drop of a few volts, largely predominate, but that rays of all velocities up to about  $2.7 \times 10^9$  cm./sec. (2000 volts) are present. The number of  $\delta$ -rays decreases rapidly as the velocity increases. These experiments have also shown that there is a close parallel between the production of  $\delta$ -rays and the ionization produced by the  $\alpha$ -particle; the number of  $\delta$ -rays varies with the range of the  $\alpha$ -particle in much the same manner as the number of ions produced in a gas.

Further, by photographing the tracks of  $\alpha$ -particles in hydrogen at a low pressure in a Wilson expansion apparatus, Bumstead obtained definite evidence of electron

\* Communicated by the Authors.

† Wertenstein, *Le Radium*, ix. p. 6 (1912).

‡ Bumstead, *Phil. Mag.* xxii. p. 907 (1911), xxvi. p. 233 (1913); Bumstead & McGougan, *Phil. Mag.* xxiv. p. 462 (1912).

*Phil. Mag.* S. 7. Vol. 1. No. 1. Jan. 1926.

trails radiating from the main  $\alpha$ -particle track \*. Only a few exceptional electrons had sufficient velocity to emerge distinctly, but there appeared to be large numbers of  $\delta$ -rays with small velocities, which formed knobs and projections on the track, giving it a ragged edge.

The track photographs which he obtained were too few and too indefinite to give any quantitative information. On the other hand, the electrical experiments gave a great deal of information concerning the velocity distribution of the  $\delta$ -rays. He did not suggest any definite theory of their origin, but proposed an empirical formula to represent the observed distribution of velocities. His observations, however, are not in disagreement with a simple theory of the production of  $\delta$ -rays, in which they are regarded as due to the collisions of the  $\alpha$ -particle with the electrons in the matter through which it passes. On this view, the maximum velocity of a  $\delta$ -ray is twice that of the  $\alpha$ -particle at the moment of impact, and such a  $\delta$ -ray is produced in the very rare event of a head-on collision. The more frequent collisions give rise to  $\delta$ -rays of low velocity, so that the number of  $\delta$ -rays increases rapidly as their velocity decreases. This theory explains in a general way the results obtained by Bumstead, but the conditions of his experiments were not sufficiently definite to provide a suitable test.

More recently C. T. R. Wilson has published some photographs of  $\alpha$ -ray tracks in air †, showing the presence of  $\delta$ -rays. He estimated that the  $\delta$ -ray of maximum range had a velocity about twice that of the  $\alpha$ -particle; it appeared, however, to be ejected nearly at right angles to the direction of motion of the  $\alpha$ -particle, and not along the direction of motion, as the simple collision theory would require. He suggested that there might be some connexion between the emission of the  $\delta$ -rays and the fact that the velocity of the  $\alpha$ -particle was about the same as the velocities of the electrons in the K-orbits of nitrogen and oxygen.

In the present experiments we have investigated the production of  $\delta$ -rays by photographing the tracks of  $\alpha$ -particles in a Wilson cloud chamber. We have directed our attention to the following points:—

- (1) The energy and direction of emission of the  $\delta$ -rays.
- (2) The dependence of the production of  $\delta$ -rays on the velocity of the  $\alpha$ -particle.
- (3) The dependence of the production of  $\delta$ -rays on the gas through which the  $\alpha$ -particle passes.

\* Bumstead, *Phys. Rev.* viii. p. 715 (1910).

† C. T. R. Wilson, *Proc. Camb. Phil. Soc.* xxi. p. 405 (1922).

The photographs have not been analysed in great detail, but, as far as our results go, we find that the simple collision theory gives a satisfactory picture of the production of  $\delta$ -rays.

§ 2. The cloud chamber was of the large type described by Wilson\*, consisting essentially of a thin brass piston moving in a brass cylinder with a glass top. The internal diameter of the glass cylindrical top was about 18 cm. and the depth 4 cm. The general method of working with an expansion chamber is so well known that no details need be given. In general, Wilson's procedure was closely followed, though some mechanical details were changed. The expansion was produced by opening a valve and so connecting the interior of the piston to a large evacuated bulb. After a suitable interval of time a battery of Leyden jars was discharged through a mercury-vapour lamp, which sent a horizontal parallel beam of light through the cloud chamber. The mechanism for opening the valve and completing the lighting circuit consisted of two heavy compound pendulums joined by a wire. They were released simultaneously: one opened the valve and produced the expansion, the other completed the lighting circuit and illuminated the tracks. The periods of the pendulums could be changed by adjusting the position of sliding weights, and the time-interval between the two events was chosen so as to give the sharpest tracks.

The tracks were photographed through the plate-glass top of the expansion chamber, by a camera vertically above. The camera was stereoscopic, the maximum apertures of the lenses being  $f/4.5$ .

Gases were introduced into the cloud chamber through a small capillary tap fitting into the curved glass side. The cloud chamber could also be connected to a manometer, on which the initial and final pressures of the gas in the chamber could be measured. In most experiments the initial pressure was atmospheric, but in some cases the pressure was reduced to about 15 cm. of mercury. The tracks were examined in four gases—air, argon, helium, and hydrogen.

Air was admitted directly from the room.

The argon was prepared from commercial argon, containing about 20 per cent. of nitrogen, by passing the gas over a heated mixture of lime and magnesium powder.

The helium was initially mixed with about 20 per cent. of

\* C. T. R. Wilson, Proc. Roy. Soc. A, lxxxvii. p. 277 (1912).

air. It was purified by passage over charcoal cooled in liquid air.

Commercial electrolytic hydrogen was used. This was found to be preferable to that generated in a Kipp apparatus from zinc and hydrochloric acid, which even after bubbling through water frequently gave a slight general fog on expansion, perhaps due to traces of hydrocarbons.

The source of  $\alpha$ -particles was the active deposit of thorium, obtained on the end of a brass rod of 2 mm. diameter, by exposure to thorium emanation. The source could be placed either inside or outside the expansion chamber. In the latter case the  $\alpha$ -particles entered the chamber through a mica window of known stopping power. The source, Th(B+C), gave two sets of  $\alpha$ -particles, of ranges 4.8 cm. and 8.6 cm., corresponding to initial velocities of  $1.70 \times 10^9$  cm./sec. and  $2.06 \times 10^9$  cm./sec.

§3. A large number of  $\alpha$ -ray tracks was photographed. Some typical tracks, illustrating the various points in connexion with the production of  $\delta$ -rays, are shown in the accompanying plates (Pls. I. and II.): the magnification is expressed relative to the length of track in the specified gas at atmospheric pressure, and the direction of motion of the  $\alpha$ -particle is from left to right.

It will be seen from these photographs that the  $\delta$ -ray tracks are exactly similar to those of slow electrons which have been described by C. T. R. Wilson, and show the characteristic curly ends accompanied by intense ionization.

A careful examination of the satisfactory photographs has led us to the conclusion that all the phenomena can be explained on the assumption that the  $\delta$ -rays are produced by collisions of the  $\alpha$ -particles with the electrons of the atoms through which they pass, provided that account is taken of the fact that, in order that the  $\delta$ -ray should be observed, sufficient energy must be communicated to it to take it clear of the main  $\alpha$ -ray column. We shall now consider from this point of view the results obtained.

The photographs show at once that the  $\delta$ -ray tracks are of varying length, and that the maximum length depends upon the gas in which the track is obtained. An examination of the early parts of the  $\alpha$ -ray tracks showed that the  $\delta$ -rays had a maximum length of 2 mm. in hydrogen, 2.6 mm. in helium, and about .45 mm. in both air and argon, all at N.T.P. (Owing to slight disturbances in the neighbourhood of the  $\alpha$ -ray source, the first centimetre of the track was seldom utilized, so that the maximum

*δ-Rays produced by α-Particles in Different Gases.* 5

δ-trail in the cases of air and argon was obtained for a somewhat smaller velocity of the α-particle than in the other cases.)

These numbers are in accord with the view that the δ-particles have a definite maximum velocity independent of the gas. Assuming that the relative stopping-power of an atom is the same for the δ-rays as for the α-particles, the ratios of the lengths of the δ-rays of maximum velocity should be:

$$\text{Air}-1 : \text{A}-1.2 : \text{He}-5.6 : \text{H}_2-4.$$

The observed ratios are :

$$\text{Air}-1 : \text{A}-1 : \text{He}-5.8 : \text{H}_2-4.4,$$

which are in sufficiently close agreement.

Further, on the view that the δ-rays are produced by collisions of α-particles with electrons of the atoms through which they pass, the maximum velocity of the δ-ray is equal to twice the velocity of the α-particle.

C. T. R. Wilson \* has found that, for electrons of ranges in air between 2 mm. and 15 mm., the range is approximately proportional to the fourth power of the velocity. For such slow electrons as the δ-rays we might expect that the range would be more nearly proportional to the cube of the velocity, a relation which holds closely for α-particles of about the same velocities as the δ-rays. Assuming the cube law, we find that the velocity of the δ-ray of maximum range 0.45 mm. is about  $3.7 \times 10^9$  cm./sec. The velocity of the α-particle was about  $1.9$  to  $2 \times 10^9$  cm./sec., so that the agreement is fairly good. A better agreement would be obtained by taking the range of the δ-ray to be proportional to the 3.5 power of the velocity, but for the purposes of this paper the cube relation is sufficiently close.

For all the gases examined the number of δ-rays per centimetre of the α-ray track remains roughly the same until about 3 cm. from the end of the α-track, when it falls off very rapidly. The number of δ-rays distinctly projecting from the initial portion of the α-track was about 10 per cm. for an initial pressure of one atmosphere, and was roughly the same in all cases. This latter observation is somewhat surprising at first sight, but it can be readily explained in a general way. The number of electrons present in a given volume at given temperature and pressure is proportional to the number of atoms in the molecule of the gas and to its

\* C. T. R. Wilson, Proc. Roy. Soc. A, civ. p. 1 (1923).

atomic number. The probability of a collision between the  $\alpha$ -particle and an electron in the gas, which will result in the electron receiving some specified momentum, is proportional to the number of electrons present, if the forces retaining them in the atom be neglected. Only such  $\delta$ -rays as project from the main  $\alpha$ -column will, however, be counted; and as the  $\alpha$ -column is of about the same thickness in different gases, the minimum range of the  $\delta$ -ray is also about the same in the different gases. The range of a  $\delta$ -ray of given velocity is inversely proportional to the number of atoms in the molecule and, roughly, inversely proportional to the square root of the atomic weight. With increasing atomic weight of the gas the number of electrons set in motion by the  $\alpha$ -particle per cm. path will increase, but the fraction of these recorded as  $\delta$ -rays will diminish.

In the following calculation we shall assume that the collisions occur as if the electrons are free and initially at rest.

Let  $E$ ,  $M$ , and  $V$  be the charge, mass, and velocity of the  $\alpha$ -particle;  $e$ ,  $m$ , and  $u$  the corresponding quantities for the electron after collision; and let  $\theta$  be the angle between the direction of motion of the  $\delta$ -ray and the initial line of motion of the  $\alpha$ -particle.

If momentum and energy are conserved in the linear motion of these two particles, then

$$u = 2V \cos \theta,$$

since  $m/M$  is negligibly small.

Thus the maximum velocity that can be imparted to the electron is twice that of the  $\alpha$ -particle. For the large distances at which these collisions take place we may assume that the particles behave as point-charges, and that the law of force between them is that of the inverse square. It can then be shown that the number of electrons projected within an angle  $\theta$  by a single  $\alpha$ -particle in its passage through 1 cm. of gas is

$$n = \pi N \mu^2 \tan^2 \theta,$$

where  $N$  is the number of electrons per c.c. of the gas, and

$$\mu = \frac{Ee}{V^2} \cdot \frac{1}{m},$$

$m/M$  being again neglected.

In our experiments the swiftest  $\alpha$ -particles had an initial range of 8.6 cm. in air at atmospheric pressure, corresponding to a velocity of  $2.06 \times 10^9$  cm./sec. Substituting this value

for V, we find  $\mu = 12 \times 10^{-11}$ , and if the particles pass through hydrogen at N.T.P.,

$$n = 2.4 \times \tan^3 \theta.$$

Now we observe as  $\delta$ -rays only those electrons which are given a certain minimum velocity such as to give a trail which projects from the  $\alpha$ -ray track. The minimum range which can be identified as a  $\delta$ -ray depends on the sharpness of the  $\alpha$ -ray track. This varies somewhat in the different photographs, but on the average the minimum range for the  $\delta$ -ray is about .15 to .2 mm. The  $\delta$ -ray of maximum range in hydrogen had a length of 2 mm. This corresponds, therefore, to a velocity of 2V. Assuming that the range of the  $\delta$ -ray is proportional to the cube of the velocity—a rule which holds for  $\alpha$ -particles of similar velocities to the  $\delta$ -rays,—we find that only those  $\delta$ -rays are definitely recognizable in the photographs which are projected within an angle  $\theta$  of the direction of motion of the  $\alpha$ -particle, where  $\theta$  is given by

$$\cos \theta = \sqrt[3]{\frac{2}{2}} = .46.$$

Hence the number of  $\delta$ -rays per cm. on the track of an  $\alpha$ -particle of velocity  $2.06 \times 10^9$  cm./sec. through hydrogen gas should be

$$n = 2.4 \tan^3 \theta = 2.4 (\sec.^2 \theta - 1) = 9.$$

A similar calculation for an  $\alpha$ -particle passing through air gives  $n = 11.5$ , and in helium  $n = 11$ .

In the case of argon we must remember that the electrons in the K orbits cannot be regarded as free, even for the purposes of this rough calculation, for the ionization potential of the K level is over 3000 volts. The K electrons must therefore be omitted, for they will only be removed from the atom by a very close collision of the  $\alpha$ -particle, and their final energy of collision will also be small. We find, then, that for argon  $n$  is about 12.

Thus to a first approximation the tracks of  $\alpha$ -particles in the four gases used will show the same number of  $\delta$ -rays per centimetre of the track. The  $\delta$ -rays will of course be much more obvious in hydrogen and helium, on account of their greater range in these gases.

In a similar way we can explain why the number of  $\delta$ -rays is approximately constant along the earlier portion of the  $\alpha$ -ray track, and falls off very rapidly in the last 2 or 3 centimetres equivalent range in air. We shall take the case of



8 Dr. J. Chadwick and Mr. K. G. Emeléus on the  
an  $\alpha$ -track in hydrogen. The number of  $\delta$ -rays projected  
within an angle  $\theta$  by an  $\alpha$ -particle of velocity  $V$  is

$$n = 2.4 \tan^2 \theta \cdot \left( \frac{V_0}{V} \right)^4,$$

where  $V_0 = 2.06 \times 10^9$  cm./sec.

The  $\delta$ -ray, in order to be observed, must have a minimum range of .2 mm. Since the velocity of a  $\delta$ -ray of range 2 mm. in hydrogen is  $2V_0$ , and assuming that the range is proportional to the cube of the velocity, the  $\delta$ -ray, if this is to have sufficient velocity to be observed, must be projected within an angle  $\theta$ , given by

$$\cos \theta = .46 \cdot \frac{V_0}{V}.$$

Writing

$$\tan^2 \theta = \sec^2 \theta - 1 = 4.6 \cdot \frac{V^2}{V_0^2} - 1,$$

we find that the number of  $\delta$ -rays per cm. on the track of an  $\alpha$ -particle of velocity  $V$  is

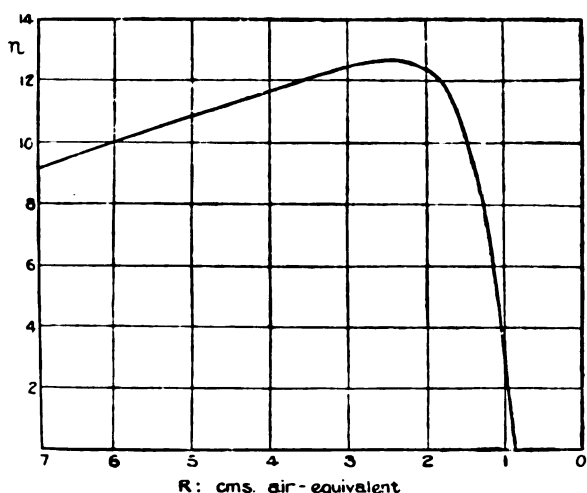
$$n = 2.4 \cdot \frac{V_0^4}{V^4} \cdot \left( 4.6 \frac{V^2}{V_0^2} - 1 \right).$$

The number becomes zero when  $4.6 V^2 = V_0^2$ . This merely expresses the condition that  $\delta$ -rays of range .2 mm. in hydrogen are the slowest that can be detected.

By taking the range of the  $\alpha$ -particle to be proportional to the cube of its velocity,  $n$  can be expressed as a function of the range. The result is shown in fig. 1, where  $n$  is plotted against the equivalent range in air, for the last 7 cm. of range. According to our calculation, the number of  $\delta$ -rays observed should increase slightly up to a point 2.46 cm. from the end of the track, thereafter falling off rapidly and becoming zero for a remaining range of 0.87 cm. This corresponds approximately to our experimental results. The initial increase in the number of  $\delta$ -rays as the velocity of the  $\alpha$ -particle decreases is so slight that a very large number of photographs would be necessary to establish it beyond doubt. The final decrease is, however, very striking, and is illustrated by comparison of figs. 1 to 6 (Pls. I. & II.) of tracks of  $\alpha$ -particles of range in air between about 2 and 7.5 cm., and figs. 7 and 8, where the range is from zero to 1.3 cm. Fig. 7 shows a single  $\delta$ -ray which is nearer the end of a track than any other so far obtained. If we suppose that the rare event of the closest possible encounter has occurred, we calculate from the range of the  $\delta$ -ray that the velocity of the  $\alpha$ -particle at this point is  $1.1 \times 10^9$  cm./sec.; calculated from the residual range, the velocity should be  $.94 \times 10^9$  cm./sec.

The first casual inspection of the photographs led us to believe that the number of long  $\delta$ -rays was disproportionately great. In examining the plates, however, there is a tendency to take those  $\alpha$ -ray tracks which show long  $\delta$ -rays as having been photographed under the best conditions, and to neglect others which, though equally sharp, show only short  $\delta$ -rays. In so doing, no account is taken of the probability variation in the distribution of the long  $\delta$ -rays. This is a very important factor, as is shown by figs. 5 and 6, where the  $\alpha$ -ray tracks were taken under identical conditions. Fig. 5 shows a number of long  $\delta$ -rays, while fig. 6 shows only short ones.

Fig. 1.



To investigate this point further, an analysis was made of the lengths of the trails of the  $\delta$ -rays. Assuming as before that the range of a slow electron is proportional to the cube of its velocity, then on the simple collision theory the number of  $\delta$ -rays of length greater than  $r$ , produced by an  $\alpha$ -particle of given velocity, should be proportional to

$$\left(\frac{R}{r}\right)^{2/3} - 1,$$

where  $R$  is the length of the track resulting from a head-on collision.

The tracks in hydrogen were examined for a portion of the track from 1.84 to 3.06 cm. from the source, that is, for an average velocity of the  $\alpha$ -particle of about  $2 \times 10^9$  cm./sec. For hydrogen at N.T.P. the maximum range of the  $\delta$ -ray

produced by such an  $\alpha$ -particle is 2 mm. It was found that 157  $\delta$ -rays had ranges greater than .62 mm., 51 had ranges greater than 1 mm., and 10 greater than 1.39 mm. These numbers are in the ratio

$$3.1 : 1 : 0.2,$$

while the theoretical ratio from the above expression should be

$$2.1 : 1 : 0.47.$$

In the case of helium the part of the track from 1.8 cm. to 8.0 cm. from the source was taken; 170 trails of  $\delta$ -rays were found of length greater than .47 mm., and of these 36 were longer than 1.03 mm. This gives a ratio of 4.7 to 1, while the theoretical ratio is 2.5 to 1.

The tracks in air and argon are not suitable for this analysis, owing to the short ranges of the  $\delta$ -rays.

In both of the above cases it appears that the number of short  $\delta$ -rays is relatively too great. The discrepancy is to be explained partly by the comparatively small number of  $\delta$ -rays examined, and partly by the method of measurement. The lengths of the  $\delta$ -rays were measured on the photographs, which are projections of a three-dimensional phenomenon. It is, of course, possible to reconstruct the track in three dimensions from the stereoscopic photographs, but this demands elaborate apparatus and would be a most arduous task. From the rough agreement with the simple theory which all our results show, it appeared to be unlikely that the results to be obtained in such a way would be a sufficient recompense for the labour involved. Moreover, for the sake of economy in photographic plates and in labour, the later photographs were not taken stereoscopically, but each half of the plate received a separate exposure.

It does not appear possible to apply an adequate correction for our method of measuring the lengths of the  $\delta$ -rays, but it can be seen that such a correction would make our results more in accord with the theory.

It may be mentioned here that the results obtained by Bumstead in his electrical measurements of the  $\delta$ -rays can be accounted for on the above theory of their origin. Bumstead measured the number of  $\delta$ -rays of different energies emitted by a metal plate exposed to the  $\delta$ -rays of polonium. As the metal plate was thick, the  $\delta$ -rays observed were due to  $\alpha$ -particles of different velocities. Taking an average velocity for the  $\alpha$ -particle, it can be shown that the number  $n$  of

δ-rays of energy greater than  $T$  is given by

$$n = \frac{a}{T} - b,$$

where  $a$  and  $b$  are constants. This relation expresses Bumstead's results rather better than the empirical formula he proposed, and the ratio  $a/b$  of the constants, deduced from his experiments, agrees approximately with the value calculated from the theory.

The next point we have to consider is the direction of emission of the δ-particles. C. T. R. Wilson came to the conclusion that in air the δ-rays had, on the average, no component of velocity in the line of motion of the α-particle. The present experiments have confirmed this for δ-rays in air and argon. In hydrogen and helium, however, the δ-rays undoubtedly have a velocity component in the direction of motion of the α-particle, in particular those δ-rays of long range. This is well illustrated by fig. 1 of Pl. I.

This difference in the apparent direction of emission is due to the fact that the scattering of the δ-rays is greater in heavy gases than in light. The scattering, even in hydrogen at low pressure, is too great to permit of any detailed correlation of the lengths of the δ-rays with their direction of emission. There is little advantage to be gained by reducing the initial pressure of hydrogen in the expansion chamber below about 12 cm., owing to the great stopping-power of the water-vapour which must of necessity be present. In the case of hydrogen at N.T.P. it can be shown that the most probable number of deflexions through an angle greater than  $45^\circ$  in the first 0.2 mm. of a 2-mm. δ-ray is 0.7, and in the first 0.3 mm. of a 0.6-mm. δ-ray it is 5.4. Thus the longer tracks should, as has been found, have a forward direction. In air, however, since the range of a δ-ray of given velocity is only  $1/5$  of the range in hydrogen, and the number of scattering electrons and the charge on the atomic nucleus are each some seven times as great, the chances of deflexion through a large angle are so greatly increased that the δ-rays will emerge from the α-track at random.

Some photographs of tracks in hydrogen were taken with a magnetic field of about 400 Gauss acting at right angles to the track, and along the axis of the expansion chamber. This field was obtained by passing a current of about 20 amperes through a coil resting on the top of the expansion chamber. The idea was to test whether any

## 12 *$\delta$ -Rays produced by $\alpha$ -Particles in Different Gases.*

appreciable number of  $\delta$ -rays was emitted in the direction of motion of the  $\alpha$ -particle. The presence of such ray would not be detected in our previous experiments. The magnetic field, however, was sufficient to bend them out of the path of the  $\alpha$ -ray and so make them visible. No change in the number of  $\delta$ -rays was noticed, indicating that even in hydrogen the scattering is sufficiently great to bring the fast  $\delta$ -rays out of the  $\alpha$ -particle track. Fig. 4 shows an  $\alpha$ -ray track taken under these conditions. The curvature of the two long  $\delta$ -ray trails is plainly seen.

One further point may be mentioned. If an electron is ejected from the K level of an atom traversed by the  $\alpha$ -particle, we should expect the corresponding X-radiation to be emitted when the atom returns to its normal state. This X-radiation will be absorbed in the gas in the neighbourhood and give rise to a  $\beta$ -ray of very short range, corresponding to the energy of the K level. Wilson has already pointed out that such  $\beta$ -rays can be observed very close to the early portion of an  $\alpha$ -ray track. In air their range is so short that only a minute globular speck is visible. In argon, however, the trail of such a  $\beta$ -ray should be about  $\cdot 3$  mm. in length, for the energy of the K level is about 3000 volts. On the other hand, this event will occur very seldom, for almost a head-on collision of the  $\alpha$ -particle is required to remove an electron from the K level of argon. We have in a few instances succeeded in observing a  $\beta$ -ray trail of this length in the neighbourhood of an  $\alpha$ -ray track in argon.

### *Summary.*

The tracks of  $\alpha$ -particles in four gases—viz. hydrogen, helium, air, and argon—have been obtained in a Wilson expansion chamber, and the production of  $\delta$ -rays along them has been studied.

As far as our observations go, the results are in accord with the view that the  $\delta$ -ray arises from the collision of the  $\alpha$ -particle with an electron in the atoms through which it passes. We assume that, for the distances involved in these collisions, the  $\alpha$ -particle and the electron behave as point-charges, and that the law of force between them is that of the inverse square.

Photographs are reproduced to illustrate the various points discussed in the paper.

II. *Models of Electron Structure, Quantum Action, and the Gravitational Field.* By W. M. THORNTON, O.B.E., D.Sc., D.Eng., Professor of Electrical Engineering in Armstrong College, Newcastle-upon-Tyne\*.

1. *Introduction.*

THE following notes were given to students of electrical engineering to suggest, by the aid of models, a picture of an electric structure of matter. They make no pretence to be more than a rough mechanical scheme based on the assumption of a vortex filament æther of which each element has torsional elasticity. The existence of such a filament implies a basic twist, in this case probably dynamic. The suggestion now made is that electrons and protons are produced by applying to it left- or right-handed twists, the effect of which is in the one case to unwind the original torsion, in the other to increase it and form a densely-packed thread. In the process, loops are formed which are either electrons or protons. Once formed in a medium with the properties of a fluid, they persist. Whittaker remarks that, of all the theories of the æther, the vortex filament or sponge has the greatest interest.

An india-rubber cord has torsional rigidity but no intrinsic twist, so that right- and left-handed loops are, with it, of the same size. The models can be made from closely-wound spirals of wire ; but though there is then a clear difference in the size of right- and left-hand loops, it is not possible to approach that which exists between protons and electrons.

The notes were given at different times, and a certain repetition of statement could not be avoided.

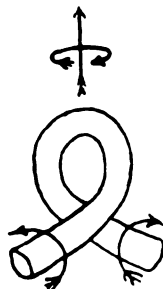
2. *Protons and Electrons.*

The form of the electric bond between nucleus and electron of the hydrogen atom is not yet known ; but it is possible to construct a model of it from the evidence of the behaviour of electric charge in motion, and through it possibly to explain quantum action. Any mechanical scheme can be made to work if the appropriate forces are assumed. In the present attempt there is only one essential, the existence of a vortex filament æther, which can be twisted or untwisted to form protons or electrons and which carries gravitational forces. The magnetic field around a moving charge is such that when the charge is positive the flux is right-handed, when

\* Communicated by the Author.

negative left-handed. This is one of the key phenomena of nature, and suggests in the strongest way that the positive unit has the physical characteristics of a right-handed screw (such as a propeller), a negative charge of one left-handed. The simplest representation of such a screw is a half-turr

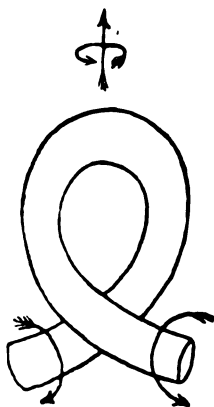
Fig. 1.



PROTON

element (fig. 1), which may be regarded as formed on a line or tube of force. Such an element moving loop first in the direction of the arrow, like a ship's log in a material medium, would by its reaction turn right-handedly or set up a right-

Fig. 2.



ELECTRON

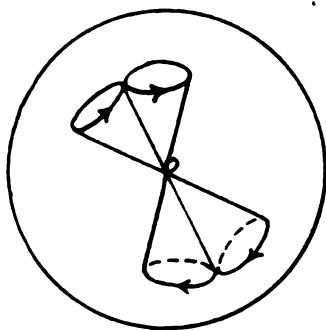
handed strain in the towing-rope, and a left-handed element (fig. 2) would turn in the reverse direction, the twist being in

each case proportional to the velocity of motion, in this way imitating the direction and magnitude of the magnetic fields around moving charges. The phenomena of steady current flow do not require anything more complex than these models, but in order that they should exist permanently as structural parts of matter and differ in size, the tubes of which they are composed must have intrinsic twist. Any such cord held at one end and turned right-handed at the other will form fig. 1, left-handed, fig. 2.

The field of force known to diverge uniformly from a point-charge can be imagined to spread from a kink of this kind by uniform enlargement of a tube of force in proportion to the radius.

To visualize a three-dimensional static twist, take a spherical ball and twist a conical element of the surface to the centre around a diameter to the opposite face until a kink forms at the centre (fig. 3). The charge would then be

Fig. 3.



an assembly of these loops, and the elements, if put together under torsion and set free, would lock into a permanent state of twist. A spherical distribution of stress from a vortex filament loop as a unit of charge seems to require that each filament should be subdivided into many elemental threads, each enlarging its section from the centre. There may truly be a finite number of tubes of force from every unit of charge. Not more than six would be stable if arranged symmetrically around the centre of a filament. In the vicinity of the centre the inverse square law could not hold.

It is a necessity of electrostatic theory that at a distance from the charge such that the inverse square law holds the field must have everywhere the same magnitude and sign.



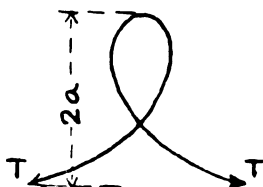
That is, every element of surface on a sphere with a positive charge at the centre has a right-hand twist of the same intensity. The only way of making a vortex filament do this is by giving it the half-turn of figs. 1 and 2. Such a configuration would obey, at some distance from the centre, all the laws of electrostatics.

### 3. *The Shape of Electrons and Protons.*

An elastic wire bent into any of the forms of the elastica curve can be rotated freely about its own axis without change of shape of the curve. Kirchhoff showed that the static elastic problem is analogous to motion about the centre line of the wire, the moment of momentum then corresponding to the couple about the axis in the static case. The vortex filament electron is stable provided that the twist is maintained. There is also in the fluid vortex case an effect which makes for stability of form that does not exist in the kinetics of solids.

When two vortex filaments cross at right angles, the fluid rotating around one axis can at the point of crossing be caught by the other vortex, and form a complete path about both, acting as an elastic band holding the branches together. It is conceivable that the permanence of an electron or proton loop may depend upon this.

Fig. 4.



The form of the loop (fig. 4) is similar to that of the simple elastica (fig. 6, p. 148, vol. i. pt. ii., Thomson and Tait, *Nat. Phil.*). From the equations given there the maximum ordinate of the loop is  $2a$ , where  $a = \left(\frac{EI}{T}\right)^{1/2}$ ,  $E$  being the elastic coefficient of bending,  $I$  the geometrical moment of inertia of the section of the filament, and  $T$  the tension in it. If, as is suggested in § 19, the filament is a spiral vortex, the tension is the rate of change of momentum along the axis.

#### 4. *Why Opposite Charges attract.*

The space around a positive charge is, in the model, considered to be in a state of right-handed twist (fig. 1). A free positive charge entering this space could not link up—the circulations are in opposite directions and could not coalesce; but such charges, if formed on the same filament or held in position by the presence of negative charges, might conceivably remain connected in equilibrium.

If one of two opposite charges is attached to a surface, it has an external field in which the other tries to turn. When a charge turns, it advances from pole to pole like a nut along a screw, away from a similar charge towards an opposite charge, setting up as it goes in the surrounding medium an induced magnetic field proportional to the velocity of motion. The model of fig. 1 would be driven loop first in such a field in one direction, that in fig. 2 loop first in the reverse direction.

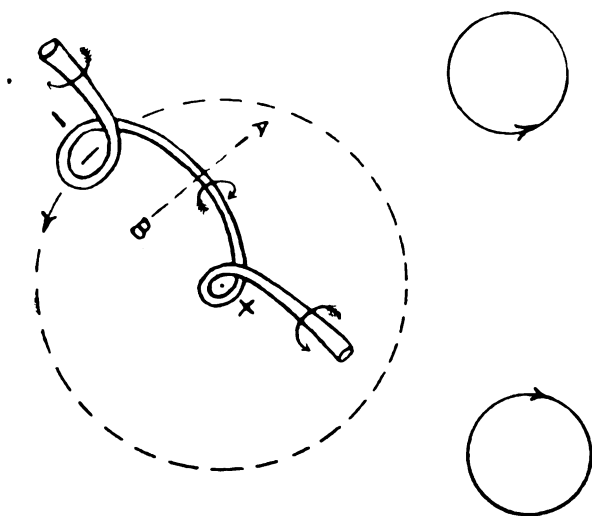
Another way of viewing this is to imagine a thin membrane (AB, fig. 5) dividing a fluid into two parts in each of which there is a vortex terminating on the membrane in a vortex sheet. If the circulation is in the same direction in the two parts and in line, withdrawing the membrane will unite the vortices, loops on which will then be attracted. If the circulation is opposite in the two parts, they will move away from one another sideways.

#### 5. *Linkage in a Hydrogen Atom.*

Right- and left-handed elements can be joined by a tube of force becoming common to both. A well-known illustration of electrostatic stress is a state of twist of tubes of force between oppositely-charged surfaces. Fig. 5 shows right- and left-hand kinks on a thread representing the attachment of positive and negative charges, which will not together be a permanent force unless either one is held in position as in a massive atom by the presence at the nucleus of other tubes of force which form the complete spherical field, or by motion in space. The revolution of a negative electron loop first about a proton as nucleus causes the loop to twist left-handed and so prevent the filament joining the charges from folding back. Unless the circulation at the crossing-point is sufficient, it would be necessary for the stability of a free atom made on such an elastic system that the negative charges should be in motion around the positive. The Rutherford-Bohr type of atom is then necessary for the stability of matter.

The nuclei of atoms are known to be extremely small and difficult to move; electrons are light and mobile. The model illustrates these properties, for if any cord or spiral of wire having a right-hand pitch is turned right-handed, the lood formed is small and tightly held; turned in the reverse direction, it is large and open. The difference in size and behaviour of the two fundamental electric charges implies that the æther has an intrinsic twist such that an added right-handed torsion causes condensation, left-handed, expansion.

Fig. 5.



In the above model the positive kink has a free end, so that a hydrogen atom can hold or capture another free electron as required on Bohr's theory for the continuous spectrum of hydrogen. The section of the filament is probably not constant, but enlarges at the centre in the manner of the lines of flow between a source and sink.

#### 6. Absence of Magnetic Field of Single Orbit.

Tubes of force, whatever their ultimate nature, cannot be bent without reaction. It follows that in fig. 5 the positive and negative charges cannot approach indefinitely, and the inverse square law which holds when the charges are so far apart that the tubes joining them are nearly straight, fails and becomes one of repulsion, according to a higher power than the second when they are close together. The inverse

square law is known to hold within the atom, but not near the nucleus.

When an electron revolves around a proton to form an atom of hydrogen, it also follows from the figures that the loops must lie in the plane of rotation. On the preceding view the revolving electron loop in a hydrogen atom tries to rotate, but is prevented from doing so more than a very small amount by the stiffness of the tube of force joining it to the nucleus. There is therefore *no magnetic field* and no continuous absorption of energy produced by such a motion, for the usual rotational strain around a negative moving charge cannot be established. The Rutherford-Bohr hydrogen atom in spite of its orbital motion is non-magnetic.

### *7. Reaction of Radiation on Atomic Field.*

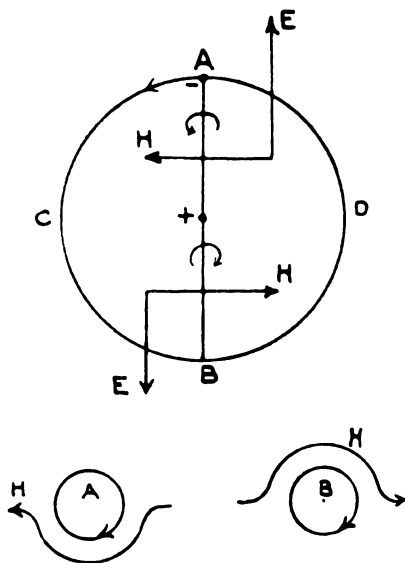
The electric field of radiation in free space is in the wave front, and the magnetic field at right angles to the electric. When the energy of such radiation is absorbed by an atom of the kind considered there are certain restrictions to change of motion of the electron. For stability of the orbit radial harmonic oscillations cannot occur, and those that under certain circumstances can occur perpendicular to the plane of the orbit have small energy and are not such that they could increase the diameter.

Absorption of energy occurs when the frequency of the incident radiation is that of rotation of the electron, or is related to it by the laws which govern the frequency of spectra; but since it is impossible to work up a radial oscillation even with synchronism, it would be necessary to give the energy quantum in one revolution or not at all. (It is, indeed, simpler to regard the relation  $W = h\nu$  as written

$W = h\nu$ ; that is, the energy which can be absorbed or radiated during one complete rotation is the same at all frequencies.) Either the absorption must take place in one period, or there must be some mechanism by which the action may be worked up without the radius slowly changing. The former alternative would seem to be ruled out, for even with the most intense natural fields of the order of 10 volts a centimetre, an electron could not acquire a quantum of energy in one revolution by the electric forces acting upon it in the wave front. In the model an electric field normal to the plane of the orbit does not influence the motion even if the periods coincide. When it is in the same plane there is no effect until the incident radiation synchronizes with

the revolution of the electron about the nucleus. There is then a series of unidirectional tangential forces repeated each half revolution—a rectified sine wave; but according to quantum action, there is no acceleration of the electron. When the orbit is in the wave front of the incident radiation, the magnetic component is at one position along a radius, after a quarter revolution across it. If the radial bond to the nucleus is a magnetic vortex filament, the influence of a stream past it is to exert a rotational drag upon it, since there is no slip, retarding the spin if below a certain speed.

Fig. 6.



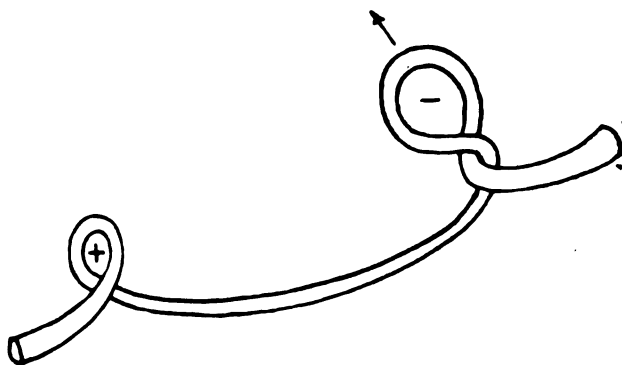
accelerating it if greater. When the radiation reaches a certain frequency, the radial bond begins to be wound up by a kind of ratchet movement—that is, its twist is increased—until it reaches a critical value, at which a change of position occurs according to quantum laws. The Poynting flux of energy is converted from the linear stream of the advancing radiation into the increased spin of the filament; but it cannot enter the filament in this way unless the electric component of the field is in the plane of the orbit. Energy is absorbed in a series of unidirectional pulses each lasting half a period. Fig. 6 illustrates this. At C and D there is no action if the radiation is polarized as

shown at E. The application of a magnetic field cannot have permanent effect on such an atomic structure unless it lasts only for a half period of rotation of an electron about the nucleus, an inconceivably small interval of time which cannot be realized experimentally.

### 8. Mechanism of Quantum Action.

In the previous section it is shown that the electron of a hydrogen atom is, in effect, *wound up* by synchronous radiation, in the sense that the twist of its bond to the nucleus is intensified. Fig. 5 now provides a clue to the quantum action in the connexion between radiation and matter, for if the twist on such a cord is increased to a certain critical amount, the negative loop makes suddenly a complete turn, taking the position of fig. 7. The increased energy of twist

Fig. 7.



causes a sudden change of position, and the radius is held constant until such a change takes place. When the incident radiation ceases, the kink returns to the normal position, so that the persistence of incident radiation is necessary for continued activation.

It is readily found by trial that such a double twist straightens the bond, so that at the moment it occurs the orbit enlarges, though under the limitations of a model not to anything like the four times greater radius required by Bohr's quantum theory. What the initial curvature of such a bond is likely to be and how far it is extensible under a straightening force is conjecture, and the kink can conceivably move along the tube, but the type of movement is that looked for.

The model explains why the incident radiation may be exceedingly weak and yet absorption take place in quanta as in the photoelectric effect ; why the effect is dependent upon frequency ; and why the radiation from an atom must always occur in quanta as the twist relaxes a revolution at a time, for radiation can only occur in quanta if *the negative kink is compelled to lie always in the same relation to the plane of motion*. There is no question of dissipation of energy by friction, and the configuration is such that the electromagnetic resistance to motion is a minimum. This is when there is no circulation through the loop of the kink. The latter places itself with its plane in that of the motion, and in this position there is no resistance. According to the model, the electromagnetic radiation arising from a sudden decrease of radius is set up by the corresponding relaxation of the filament connecting proton and electron. The change of the electrostatic energy of the two charges is transmitted into space by the equal magnetic impulse in the circulation of the filament joining them. This magnetic movement is at right angles to the electric field between the charges, and therefore in the right position to start a wave motion of regular type.

The photoelectric emission of electrons from metals in quanta relations is a trigger effect. The outer electrons of atoms in metals are very closely packed, and in a state of mutual repulsion such that the stability of some of them is easily disturbed. Anything that does this may result in electrons being set free, and this is continually happening. The magnetic field of radiation, or that of an electron passing close to or through an atom, resembles in its effect on the filaments between protons and electrons a hand swept over the strings of a harp, throwing them into lateral vibration and possibly snapping one, the released energy of which is much greater than that required to break it. A broken string is analogous to the release of an electron with the collapse of the bond to the nucleus. The energy of the released electron comes from the atomic structure, not much from the incident radiation.

### 9. *Vibrations with Zero Energy.*

In the development of the Planck's radiation formula it is considered that of  $M$  vibrations,  $N$  have zero energy.

The fraction  $\frac{M-N}{N}$  is that proportion of the wh

number which have any energy; and this is proved to be  $e^{-eRT}$ , where  $e$  is a quantum,  $R$  and  $T$  the gas constant and temperature.

From this it follows that "in a red-hot mass of iron less than 1 per cent. of the red vibrations have any energy; the remaining 99 per cent. are perfectly dead" \*.

Of all the statements in the quantum theory this is perhaps the most difficult to reconcile with the old view. Interpreted by the model, it means not that the vibrations are dead, but that it takes 99 vibrations to get one quantum of energy absorbed. It takes so many revolutions or alternations of the field of radiation to wind the electron loop up to the point where it turns over suddenly once to form fig. 7. There are 99 vibrations in which there is no evidence of absorption or radiation of energy.

#### 10. *Mass of Protons and Electrons.*

On the vortex sponge theory, or any theory in which an æther at rest is postulated of which protons and electrons are individual parts, matter is in continuous flux. No proton or electron in motion is ever composed of the same æther for more than an inconceivably small portion of time. If the laws of vortices hold for the æther filaments considered, a region of small tightly-bound loops has higher angular velocity and greater resistance to motion than one in which the section is greater or the loop with less curvature—that is, its inertia is greater. A large open loop moves easily by comparison. The difference in mass and dimensions of the two charges is so great that the apparent elastic constants of the filaments must differ greatly in degree from those of ordinary matter. If they could be determined from the properties of atoms on this or any model, they might give a clue to the value of the absolute dielectric constant of free space.

The suggestion that a quantum consists of energy stored by a second further twist of a filament as in fig. 7 has, in consequence of the above, the effect that the added twist increases the apparent mass of an electron or gives it to some extent the character of a positive charge; and this may account in part for the departure of atomic weights from integers. If this were so, it would account for the weakening of the bond to the nucleus and the enlargement of the orbit according to a square law. Presumably a point would be

\* Jeans, 'Report on Radiation,' p. 31.

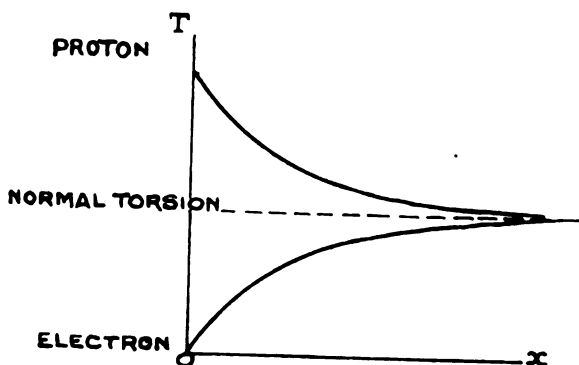


reached where the attraction to the nucleus would be unable to hold the electron so that there would be a limit to the size of the hydrogen atom. Intense radiation would seem to be the only controllable means of splitting a hydrogen atom.

### 11. Mass of Protons and Electrons (continued).

The view advanced in the previous sections is that the fundamental charges differ in the first place in the direction of a twist superposed upon a normal torsion of an æther filament, that of the proton being the greater, that of the electron less. This twist in a single thread must be regarded as greatest at the centre, as in a waterspout or vortex, or at the surface of a hollow vortex. Assuming the intrinsic torsion to be  $T_0$ , and the maxima of the added or subtracted twists to be the same, as they must be if connected by a

Fig. 8.



common tube, and equal to  $T_1$ , the twist at any distance  $x$  from the axis of the filament, assumed straight, is  $T_0 - T_1 e^{-\alpha x}$  in the case of the negative or less dense charge,  $T_0 + T_1 e^{-\beta x}$  for the dense proton filament (fig. 8).

Near the axis the ratio of these is  $\frac{T_0 - T_1}{T_0 + T_1}$ .

This, other than direction of twist, is the essential difference between them.

If, then, we may assume that this is the cause of difference of mass and that the ratios of their masses are the same as of their concentration or vorticity,

$$\frac{T_0 + T_1}{T_0 - T_1} = 1845, \quad \text{or} \quad T_1 = \frac{1844}{1846} \cdot T_0.$$

The meaning of this near approach to unity is that the left-handed twist, to which the structure of the electron is supposed to be due, almost negatives the normal twist  $T_0$  so that the æther in the electron is held in very light torsion. An electron has more form than substance. The same twist that causes so light and mobile a structure makes, on this assumption when reversed, one 1845 times as massive. Since  $T_1$  is nearly equal to  $T_0$ , the torsion of the proton is *double* that of the normal filament. On the analogy of ordinary matter the elastic coefficient of the æther is such that doubling the twist of an element of it has the same effect as doubling its density. An electron is a region of lowered density, a hollow or nearly unstrained thread approaching Kelvin's hollow spiral vortex filament.

The exponential terms are introduced, for at great distances the added spin vanishes, leaving only the normal torsion  $T_0$  in free æther filaments.

### 12. *Why Electrons are freer than Protons.*

On the vortex filament theory, the more intense the circulation the greater the "suction"—that is, the field in the immediate neighbourhood of a positive charge is more intense, because of its smaller size, than that around a negative charge. In all cases beyond that of the hydrogen atom where the bond is the simplest conceivable, the presence of the diffused field from other outer electrons attached to the nucleus makes it easier for an electron to escape; and in metals one must regard the forces of repulsion from these electrons as so high that they escape and interchange with ease.

### 13. *Cohesion and Gravitation.*

Since all matter is now found to be electrical, cohesion and gravitation must be capable of interpretation by models of this kind. On the assumption that the bond from nucleus to electron does not utilize all the tubes of force from each, or that, as in fig. 5, there is a free end to the proton, the field from one atom to another which causes cohesion is merely the drawing together of molecules so that the vortex filaments of their atoms become common to both; and since there is no restriction to the number which can be attached in line, we may regard the matter of the earth as a succession of molecules or of atomic nuclei threaded on common filaments reaching to the centre, each nucleus contributing to the inertia of the whole, and each filament being capable of sustaining the load or tension of all its atoms.

In order that gravitation should be explained in this way, the filaments must be considered to be capable of infinite extension, not like an elastic cord, but in the same way as a bullet passing through the air causes a spin of the latter around it so we may regard the movement of a planet from a sun as setting up as it goes to its orbit a state of an enormous number of persistent twists which in this case cannot relax except by the return of the satellite. Thus space near the sun is not undisturbed æther, but a mass of threads permanently twisted by reason of the gravitational field of each planet. Such a state of the medium, though not actually constituting matter, is an extension of it, and might affect the passage of light at grazing incidence through it.

Gravitational tubes of force need not end on solid matter : they can terminate by dilution in the vortex filaments of free space. An isolated body from interstellar space could then carry with it its own gravitational field and be affected by another body which it may pass. The essential torsions in the æther around such a free body are a consequence of the original cataclysmic twist to which in § 18 the origin of the body is attributed.

The vortex filaments of which the kinks of figs. 1 and 2 are part are the means by which gravitation is transmitted. Electricity is, in fact, a singular form of gravitational space ; only in interstellar space is the æther an unstrained vortex sponge, and even there it is not at rest, for radiation is continually passing and each thread is in continual spin about its axis.

#### 14. *Chemical Combination and Gravitational Force*

Most of the chemical and physical properties of an atom depend upon the outer electrons, but gravitation, depending only on mass, upon the protons. In the model of fig. 5 there are free ends to the electron and proton loops. The former is the chemical bond, the latter the gravitational. Gravitational forces are transmitted through matter by links in a chain. A gravitational field at the surface of a body is attached to the free end of protons which are linked to their electrons. These in turn are attached to other atoms by the chemical bond—that is, by interlinking of orbits or by an electron becoming attached to two nuclei. Fig. 9 illustrates how such forces may be transmitted through matter.

The bonds of chemical combination are part of the means by which gravitational force is transmitted in solids ; another part is cohesion. In the organic world cohesion is largely the interlocking of cells, in the inorganic world of crystals. Liquids and gases experience gravitational forces by the free ends of their proton loops engaging with, breaking away from, and re-engaging gravitational tubes of the body to which they are attached in space.

### 15. *Existence of Electrons in the Nucleus.*

There is no experimental evidence of the existence of free units of positive charge except in the rare and transient case of atoms expelled from a radioactive body, and even then there may be electrons in the nucleus. This implies that they have so great a structural affinity for electrons that they always have one at least attached to them ; and since free electrons exist, it seems improbable that positive units at rest ever can be free—they are all absorbed in the structure of matter. But it is possible from the model for an electron to be linked to two protons (fig. 9) and in this way be held in

Fig. 9.



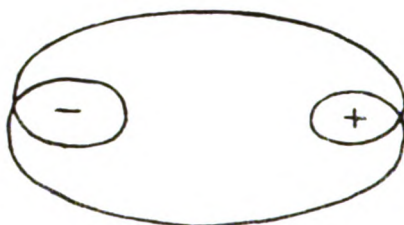
the nucleus, though under such intense force, due to the high curvature of the "elastica" bond, that when they are expelled by the shock of high velocity bombardment or in radioactivity they emerge with great speed. It is conceivable that a simple atom may be formed, like a benzene molecule, of a chain of these charges forming a closed ring. Such a nucleus would be very inert, since it has few, if any, divergent lines or tubes of force.

Although positive or negative charges, if free, repel those of the same sign, yet one can conceive a series of them formed on the same filament in the same way that such a series of loops can be formed on an elastic cord, all of the same right- or left-handed twist. In this way an extremely dense body might be formed with few or no electrons.

16. *A Model of the Helium Atom.*

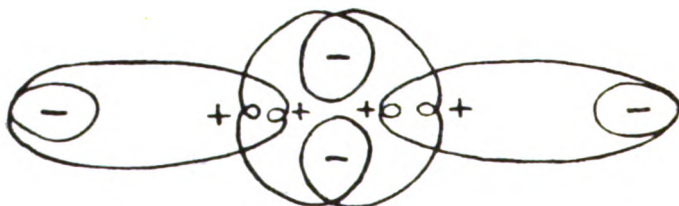
A helium atom differs greatly in physical and chemical properties from hydrogen. If a hydrogen atom formed a closed loop (fig. 10) it would have little or no chemical

Fig. 10.



affinity as measured by the existence of free active ends to its filaments. For this reason the structure of fig. 5 is preferable. But a helium atom is so entirely inert that a model with linked closed loops is suggested (fig. 11).

Fig. 11.



Here the positive charges in the nucleus are drawn together by the centrifugal pull of the outer electrons, but are held apart by their own repulsions forming a stable system; and since there are also two negative electrons in the complete four-proton nucleus, the atom would be composed of two large loops with their positive charges inside and two hydrogen atoms in series forming the smaller inner loop. The radius of a helium nucleus is, in fact, equal to the diameter of a negative electron as the model suggests.

The outer electrons can be lost without the disintegration of the nucleus, for the two inner protons move nearer to the centre when they go. The atom in this state may have intense chemical activity since it has unsaturated bonds. Could, for example, molecules of helium chloride ever be formed by exposing chlorine to radioactive action?

The two-group spectrum of helium has been traced to the

two outer electrons moving in orbits slightly inclined to one another. The model of fig. 11 would give such a spectrum, for loops so linked cannot lie in the same plane everywhere, though the outer loops might nearly do so.

#### 17. *Radioactivity and the Helium Atom.*

The projection of a helium atom from the nucleus of a radioactive body implies the existence of forces in it resembling those of static or dynamic deformation suddenly released. Atoms of the hydrogen type can pack into a symmetrical system easier than the suggested helium atom with interlinked loops. It is conceivable also that in the packing of a dense atom like radium the helium links may be displaced so that the outer electrons are not exactly opposite. There is then a resultant force away from the centre. A complex nucleus of such units resembles those puzzles composed of loose metal parts which in one slightly strained position can be separated.

A further possibility is that the helium atom is normally incomplete—that is, with some of its loops open and attached to other charges in the nucleus. At some stage of the slow rearrangement of charge that undoubtedly occurs these ends break from their hold and close. At this moment the helium atom becomes a foreign body having no part in the structure, and is expelled by the closing up of the bonds around it in their effort for symmetrical spacing.

#### 18. *Mode of Generation of Electric Charges.*

If an element of volume of a vortex filament æther is thrown into intense rotation *as a whole*, the circulation of some filaments will be increased, of others diminished. At a critical value of this added twist, loops are formed in the manner of § 1, lock into shape, and the two kinds of electricity appear, combining immediately to form matter. Immense spiral turbulence or the electric and magnetic fields of radiation of great intensity are possible sources of the generation of matter as known to us. A new world may leap into being by an intense swirl in the æther causing its filaments to precipitate out as electricity and matter to form a new spiral nebula or star. It is a consequence of such an action that equal numbers of protons and electrons should be produced; but it is possible that before such newly-formed units could combine, the electrons might be swept away by the terrific motion. In such a case a body of immense density would be formed; and since there would

be no electrons to vibrate and radiate, the star or nebula would be dark. It would be stable, for it is formed *in situ* and not assembled. Once formed, the protons are inextricably tangled and could not well escape; but if they should, the star would explode with great disturbance of the æther and liberation of energy as light and heat to form a "nova."

### 19. *Faraday's Law of Electromagnetic Induction.*

The hydrogen atom is the unit of matter—a proton and electron connected by a common bond. Such a unit moved across a steady magnetic field is polarized in the sense that there is a radial electric field; but there is no corresponding movement of the charges except under quantum conditions. The influence of the induced electric field can be illustrated by its action in fig. 5. The internal field is there shown as the twist of the common tube of force. An induced field either increases or decreases this twist, and should therefore have a rotational component (Heaviside's  $\mathbf{G}$  in  $\text{curl } \mathbf{E} = 4\pi\mathbf{G}$ ). According to this the intrinsic twist of æther filaments is identified as a magnetic circulation probably very slow, as shown by Lodge, and an electric charge is merely a kink in a magnetic vortex filament. But in order that there should be a true magnetic circulation, there must be a displacement equivalent to a current along the axis of the filaments. If the motion of a filament were spiral this would be satisfied; an axial component of motion combined with a circulation around it. Faraday's Law of Electromagnetic Induction reduces in the model to the statement that when an element of space and a magnetic field are in relative motion, the vortex filaments experience a superimposed twist, screwing, if matter is present, the protons to one side, the electrons to the other.

### 20. *A possible Magnetron or Unit of Magnetism.*

The electric current along the axis of a vortex in the electromagnetic analogue of the liquid case is the same in both electron and proton, since these can be linked by a common tube. This current in passing around a loop has a definite field linked with it. Is such a unit of magnetism the suggested magneton? The fields of such loops are part of the flux around a magnetic vortex filament, and are extremely small and local. A single hydrogen atom might have a stray field from the proton loop to the electron, but most of the flux would be close to the loops. The sign of the flux through the proton loop is the same as that which would be caused by the spin of the electron about its line of motion if

it could occur. The sign of the electron loop flux is opposite to that of the proton, so that, except for any stray field connecting the two, the atom would be non-magnetic.

For a substance to be magnetic there would have to be the same orientation of a large proportion of densely-packed protons, and from the small range of magnetic materials it is probable that such orientation is only possible in a few cases. From fig. 3 it will be seen that, according to the model, a magnetic field should have the effect of rotating a free charge in a plane at right angles to the field. On ordinary matter containing equal numbers of electrons and protons a magnetic field has no resultant effect.

### 21. *Diameters of Vortex Filaments.*

An estimate of the order of the diameter of an æther filament may be made from the dimensions of electrons on the assumption that they are loops of the kinds considered.

The constant  $\alpha$  in fig. 4 is  $\left(\frac{EI}{T}\right)^{1/2}$ . For a solid round wire

$I = \pi r^4/2$ , and for a vortex filament is of the same order. Analogy with a hollow vortex is more difficult. The radius  $r$  of the filament has two limiting sizes—that of the electron larger, of the proton smaller, than the normal filament of free æther. These are determined by the size of the loop, the overall dimensions of which are  $2\alpha$ . By comparison with loops on wire spirals the diameter of the filament cannot well be greater than  $0.5\alpha$ , and a radius of  $0.25\alpha$  can be taken as a first estimate.

The size of the helium nucleus is about  $4 \cdot 10^{-13}$  cm., and in this there are two electrons. Unless the size of an electron varies with the intensity of the forces acting on it, its diameter there is of the order  $2 \cdot 10^{-13}$  cm. Taking this as  $2\alpha$ , the larger possible radius of a filament is not greater than  $2.5 \cdot 10^{-14}$  cm. There are in the helium nucleus four protons. If these are grouped as in fig. 11 their maximum diameter is  $10^{-13}$ , but they are probably much less.

Taking, in fault of a better supposition, the mass of a charge to be inversely proportional to its volume, the ratio of the mass of a proton to that of an electron is  $(I_e/I_p)^{3/2}$  and  $r_e/r_p = 1845^{1/2} = 3.5$ .

According to this the effective radius of the filament of a proton is  $1/3.5$  that of an electron, or at most  $0.7 \cdot 10^{-14}$  cm., the elastic constant and tension being the same.

The radius of a filament of free æther is between these. If the absolute density of æther is the mean of that of electrons and protons, the diameter of its filaments is on the above argument about  $2 \cdot 10^{-14}$  cm.



III. *A Method for Determination of the Adsorption of Ions on Colloidal Particles by means of Donnan's Membrane Equilibrium Theory.* By HERMAN RINDE \*.

DONNAN'S Membrane Equilibrium Theory can be stated as follows: If there are on one side of a semipermeable membrane (inside the membrane) non-dialysable ions, this will lead to an unequal distribution of a dialysable electrolyte on both sides of the membrane, so that at equilibrium the activity of the electrolyte inside the membrane is equal to the activity of the electrolyte on the other side of the membrane (outside the membrane). If there is only one dialysable electrolyte with two monovalent ions, the activity is equal to the product of the activities of both ions. If  $a_{1+}$   $a_{2+}$  are the activities of the cations inside and outside the membrane, and  $a_{1-}$  and  $a_{2-}$  the activities of the anions, we have

$$a_{1+} a_{1-} = a_{2+} a_{2-} \quad . \quad . \quad . \quad . \quad (1)$$

Let  $y$  be the concentration,  $f_y$  the activity coefficient for the cations inside the membrane,  $w$  and  $f_w$  the same expressions for the anions, and let  $z$  denote the concentration of the nondialysable ions. Then

$$a_{1+} = f_y y ; \quad a_{1-} = f_w w. \quad . \quad . \quad . \quad . \quad (2)$$

As the liquid inside the membrane must be electrically neutral, we obtain, if the nondialysable ions are assumed to be anions,

$$y = z + w. \quad . \quad . \quad . \quad . \quad (3)$$

Thus

$$z = \frac{a_{1+}}{f_y} - \frac{a_{1-}}{f_w} \quad . \quad . \quad . \quad . \quad (4)$$

Substituting from formula (1)

$$z = \frac{a_{1+}}{f_y} - \frac{a_{2+} a_{2-}}{f_w a_{1+}} \quad . \quad . \quad . \quad . \quad (5)$$

The activity of the different ions is not exactly known †, but for hydrochloric acid it is probable that the difference in the activity coefficients between the hydrogen and the chlorine ions is not large. It may therefore be permissible to calculate with the same activity coefficient for both these ions. Further, if the concentration of the nondialysable ions is

\* Communicated by Prof. F. G. Donnan, F.R.S.

† Lewis and Randall, 'Thermodynamics,' p. 379.

low, the activity coefficients  $f_y$  and  $f_x$  can be replaced by a mean value  $f$ , which is equal to the activity coefficient of HCl outside the membrane. As it is supposed that there is no other electrolyte than HCl outside the membrane, we can write

$$a_{2+} = a_{2-} = a_2,$$

and if  $a_1$  is written instead of  $a_{1+}$ , formula (5) can be simplified to :

$$z = \frac{a_2}{f} \left( \frac{a_1}{a_2} - \frac{a_2}{a_1} \right). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If the nondialysable ions are cations, this formula becomes

$$z = \frac{a_2}{f} \left( \frac{a_2}{a_1} - \frac{a_1}{a_2} \right). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

It is therefore possible to calculate the concentration of the nondialysable ions from the activity coefficient for HCl and the experimental determinations of the hydrogen ion activity inside and outside the membrane. In this research I have used the values of the activity coefficient from Lewis and Randall ('Thermodynamics,' p. 336), and from a curve with  $f$  as ordinate and ionic activity as abscissa, values of  $f$ , corresponding to the hydrogen ion activity  $a_2$ , can be obtained. The values of  $f$  and  $a$  used are reprinted in Table I.

TABLE I.

$a.$	$f.$	$a.$	$f.$
0.0005	0.99	0.043	0.86
0.001	0.98	0.081	0.81
0.002	0.97	0.157	0.78
0.005	0.95	0.230	0.77
0.009	0.92	0.305	0.76
0.018	0.89	0.381	0.76

This Membrane Equilibrium Theory has been experimentally tested by Donnan and his collaborators, J. Loeb, Procter and Wilson, and many others\*. In all these researches

\* For a complete bibliography on the subject see W. E. Garner, "Membrane Equilibria," Fourth Report on Colloid Chemistry, p. 121: London, 1922; F. G. Donnan, "The Theory of Membrane Equilibria," Chemical Reviews, vol. i. No. 1, p. 73 (1924).

it is considered that an ion is nondialysable only when its own dimensions are so large that it cannot pass through the pores of a semipermeable membrane. One can, however, imagine that a dialysable ion, through adsorption to a nondialysable colloidal particle, becomes nondialysable.  $z$ , in the preceding formulæ, signifies then the concentration of adsorbed ions. As is known, the colloidal particles of a great many colloids are electrically charged, and it is supposed that this charge and the stability of the colloid are due to the adsorption of ions.

Donnan has shown that there must exist across the membrane a potential difference (the membrane potential), and that the value of this is

$$E_m = \frac{RT}{F} \log \frac{a_1}{a_2}.$$

Formula (7) can therefore be transformed to

$$z = \frac{a_2}{f} \left( e^{\frac{E_m F}{RT}} - e^{-\frac{E_m F}{RT}} \right). \quad . \quad . \quad . \quad (8)$$

Thus, from the membrane potential and the concentrations of the ions outside the membrane, it is possible to calculate the quantity of adsorbed ions.

The osmotic pressure inside the membrane against the solution outside is equal to the sum of the osmotic pressure of the colloidal particles, and the difference in the osmotic pressures of the ions inside and outside the membrane. If dissociation is complete and the concentration of the colloidal particles is  $c$  ( $c=1$  when the number of colloidal particles per litre = Avogadro's constant), the osmotic pressure becomes

$$P = RT(c + w + y - 2x). \quad . \quad . \quad . \quad (9)$$

Supposing that the osmotic pressure of the colloidal particles is small compared with the difference in the osmotic pressures of the electrolyte on both sides of the membrane, formula (9) can be simplified to

$$P = RT(w + y - 2x). \quad . \quad . \quad . \quad (10)$$

In order to investigate whether my assumption that adsorption of ions on colloidal particles causes such an unequal distribution of an electrolyte, the present research was carried out. For the purpose of freeing the problem from every complication, I had to choose, as a colloid, one that was not a colloidal electrolyte, and as dialysable

electrolyte, one which certainly did not give any chemical reaction with the colloid. I chose as colloid colloidal sulphur, and as dialysable electrolyte HCl. From Odén's \* and Freundlich and Scholz's† researches, it is likely that sulphur particles hold ions adsorbed. By means of fractional coagulation it is possible to get fairly uniform sulphur sols, which are stable in rather concentrated acids and therefore could be supposed to be suitable for such a research.

The sulphur sols were prepared according to Raffo's‡ method from conc.  $\text{Na}_2\text{S}_2\text{O}_3$ -solution and conc.  $\text{H}_2\text{SO}_4$ . The colloidal sulphur formed was reversibly coagulated by conc. NaCl-solution, and the coagulum, separated from the liquid by centrifuging, was dissolved in lukewarm water. This operation was repeated until the liquid above the coagulum gave a neutral reaction. The sulphur was then dissolved in a large volume of water, so that the sulphur concentration was about 5 gm. per litre, and this sol (the original sol) was divided up into uniform sols by fractional coagulation. To the sulphur sol was added such a quantity of 1-normal NaCl solution that the NaCl concentration in the sol was 0.10 N. The coagulated sulphur was centrifuged off, dissolved in water, and this sol was marked ( -0.10). In this way the original sol was divided up into five sols, marked: ( -0.10), (0.10-0.20), (0.20-0.30), (0.30-0.40), and (0.40- ). These sulphur sols were then repeatedly coagulated with conc. HCl until an analysis showed that they did not contain Na ions.

These sols were rather acid, and I tried to free them from acid by dialysing through collodion bags, which I prepared by pouring very concentrated collodion inside an Erlenmeyer flask and drying the collodion film hard. On the collodion bag was fixed a narrow glass tube which acted as an open manometer, from which the osmotic pressure of the sulphur sol against the liquid outside could be read. The dialysing process was continued during nearly two months, the water outside the membrane being changed every second day. I found that after this time acid still dialysed out from the sulphur sol, but at the same time irreversibly coagulated sulphur was formed. It is therefore probable that sulphur particles which lose all of their adsorbed ions coagulate irreversibly.

I tried at first to determine the hydrogen ion activity with an ordinary hydrogen electrode, but this was impossible, since

\* Sven Odén, "Der Kolloide Schwefel," *Nov. act. reg. soc. scient. Upsala*, ser. 4, iii. No. 4 (1913).

† H. Freundlich and P. Scholz, *Koll. Beih.* xvi. p. 234 (1922).

‡ M. Raffo, *Kolloid Zeit.* ii. p. 358 (1908).

the electrode became poisoned from the colloidal sulphur, and the values of the E.M.F. were neither constant nor reproducible. Neither was it possible to determine  $p_H$  in the sulphur sols by means of indicators, as they were adsorbed on the colloid and gave a colour to the solution which was not composed of the added colours of the sulphur sol and the indicator. Fortunately, however, I found that Biilmann's quinhydrone electrode could be used for determination of the hydrogen ion activity in sulphur sols.

I have in my experiments used the following three cells:—

1. Quinhydrone electrode Solution inside the membrane	KCl sat. sol.	Calomel electrode,
2. Quinhydrone electrode Solution outside the membrane	KCl sat. sol.	Calomel electrode,
3. Calomel electrode	Solution outside the membrane    Solution inside the membrane	Calomel electrode.
Membrane.		

Supposing that the E.M.F.'s of these cells are  $E_i$ ,  $E_0$  and  $E_m$ ,  $a_1$  and  $a_2$  the hydrogen ion activity inside and outside the membrane, and that

$$p_{a_1} = \log \frac{1}{a_1}, \quad p_{a_2} = \log \frac{1}{a_2},$$

the following equations are applicable if the saturated calomel electrode is used and the temperature is  $18^\circ$ :

$$E_i - E_0 = E_m \text{ (the membrane potential),} \quad (11)$$

$$p_{a_1} = \frac{0.4510 - E_i}{0.0577}, \quad \dots \dots \dots (12)$$

$$p_{a_2} = \frac{0.4510 - E_0}{0.0577} \quad \dots \dots \dots (13)$$

The E.M.F.'s of both the first cells increased rapidly during the first half-hour after the cell was built up; and then became constant or fell slowly. I have in my results used the maximum value of the E.M.F. As a rule, the more acid the solution contained the more constant was the E.M.F. I failed very often in measuring the membrane potential  $E_m$  and could find no reason why. When, however, I got a constant value for  $E_m$ , it checked well with  $E_i - E_0$ , as the following tables show. A necessary condition was that during the measurement of  $E_m$  the pressure from the solution inside against the solution outside the membrane must be the same as the osmotic pressure at equilibrium.

The experiments were carried out in the following manner. The collodion bag (volume 200 c.c.) and the manometer were filled with a dialysed sulphur sol and put into a three-litre beaker with diluted acid. After about 48 hours the osmotic pressure had become constant, showing that equilibrium was reached. During the time of dialysing, stirring was often accomplished by pressing the walls of the collodion bag together. After 72 hours dialysing, 5 c.c. of the sulphur sol were taken out from the collodion bag by means of a pipette, saturated with quinhydrone, and  $E_i$  was measured. In place of the 5 c.c. which were taken out, the collodion bag was refilled with another 5 c.c. pure sol, so that the concentration of sulphur inside the membrane was constant. I have calculated that during one series of experiments with a sol, the sulphur concentration varied less than one per cent. The activity  $a_2$  of the hydrochloric acid outside the membrane was also measured with Biilmann's quinhydrone electrode. The acidity outside the membrane was then increased, and after another three days a new reading was taken. This procedure was continued until the acidity was so high that  $E_i$  and  $E_0$  attained the same value within experimental error. Even at this concentration of the acid no coagulation could be traced. The last experiments in the following Tables IV. and V. were made in order to find whether I got the same values for  $E_i$ ,  $E_0$  and the osmotic pressure when the membrane equilibrium was reached by decreasing the acidity outside the membrane. The values obtained in these cases are, within the experimental error, the same as when the acidity is increased.

For eliminating the liquid junction potential I used a saturated KCl solution. It is obvious that this potential can be neglected, because if there were a liquid junction potential I should never have obtained  $E_i - E_0 = 0$ , but certain positive or negative values which were equal to the liquid junction potential.

The sulphur concentrations in the sols were determined by oxidation of the sulphur with bromine, and the sulphuric acid was weighed as  $\text{BaSO}_4$ . The sulphur concentrations were:—

0.10-0.20 .....	14.75 gram S per litre.
0.20-0.30 .....	7.99 " " " "
0.30-0.40 .....	29.17 " " " "
0.40- .....	34.21 " " " "

The sol ( -0.10) showed a very small membrane effect, and no measurements were made on this.

Fig. 1.

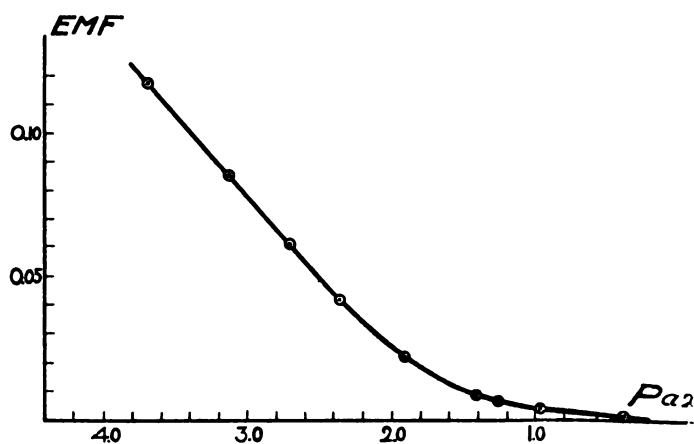
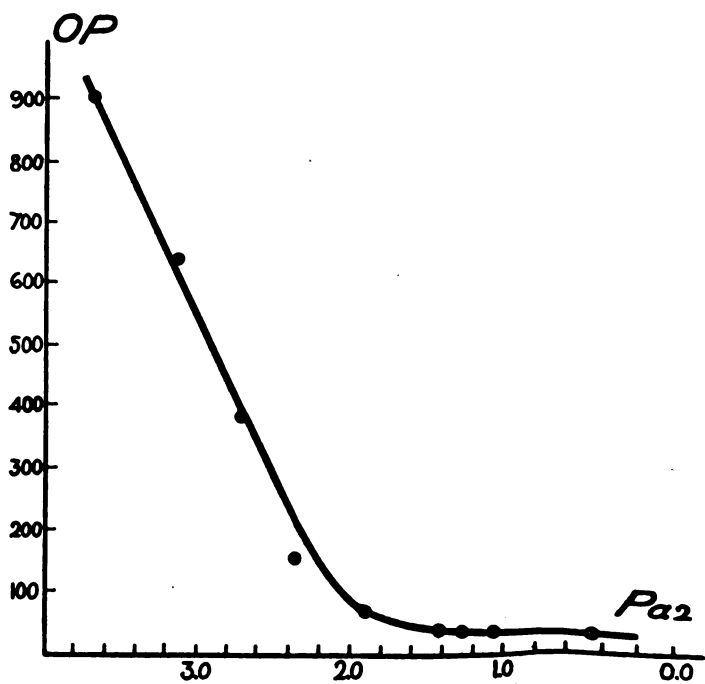


Fig. 2.



The results are reproduced in Tables II.-V., and in figs. 1 and 2 are given the values for the membrane potential ( $E.M.F. = E_i - E_o$ ), and the observed osmotic pressure in mm.  $H_2O$  (O.P.) plotted against the negative logarithm of the hydrogen ion activity outside the membrane ( $p_{a_2}$ ). The numerical values are taken from Table V.

The membrane potential has its highest value when the acidity of the colloid is small, decreasing when the acidity rises and approaching zero.

The curve for the osmotic pressure has the same shape as the membrane potential curve. It is, however, approaching not zero, but a certain positive value. It can be supposed that this pressure is due to the colloidal particles themselves and proceeding from this assumption it would be possible to calculate the size of the sulphur particles. If such a calculation is carried out, one finds that the sol (0.10-0.20) would contain the smallest particles and the sol (0.40- ) the largest. An examination of the colloids in the ultramicroscope shows that the sol (0.10-0.20) contains very large particles and the sol (0.40- ) only amicros. The simple assumption that this minimum pressure would be the pressure from the colloidal particles only is therefore incorrect. The column  $P_{cal}$  in the tables contains calculated values of the osmotic pressure according to formula (10), in the cases where complete ionization could be supposed. This value is many times larger than the experimentally determined osmotic pressure. A similar relation has been found by E. and H. Hammarsten\* in their research concerning the osmotic pressures of certain electrolytes with large molecules. These authors advance a theory according to which a colloidal ion and an ordinary ion act osmotically as one particle when the distance between them is less than a certain value  $b$ , and as two particles when this distance is larger than  $b$ . This theory is also applicable in the case of the sulphur sols. However, from my experiments I can only draw the conclusion that it is impossible at this time to calculate either the size of the particles or the membrane equilibrium, from the osmotic pressure.

In the tables,  $S$  is the concentration of sulphur in grams per litre, and  $z/S$  is therefore the concentration of monovalent ions adsorbed on each gram of sulphur. In fig. 3,

\* Einar and Harald Hammarsten, *Arkiv för Kemi Mineralogi och Geologi*, Bd. viii. No. 27, p. 1 (1923).



TABLE II.

P.	P <sub>cal.</sub>	E <sub>i</sub> .	pa <sub>1</sub> .	a <sub>1</sub> .	E <sub>0</sub> .	pa <sub>2</sub> .	a <sub>2</sub> .	f.
215	309	0.2855	2.867	1.36 . 10 <sup>-3</sup>	0.2055	4.253	5.58 . 10 <sup>-5</sup>	1
100	227	0.2777	2.829	1.48 . „	0.2490	3.499	3.17 . 10 <sup>-4</sup>	1
24	163	0.3015	2.590	2.57 . „	0.2845	2.884	1.31 . 10 <sup>-3</sup>	0.98
20	...	0.3300	2.096	8.02 . „	0.3257	2.171	6.75 . „	0.93

TABLE III.

P.	P <sub>cal.</sub>	E <sub>i</sub> .	pa <sub>1</sub> .	a <sub>1</sub> .	E <sub>0</sub> .	pa <sub>2</sub> .	a <sub>2</sub> .	f.
284	378	0.2897	2.794	1.61 . 10 <sup>-3</sup>	0.1997	4.353	4.44 . 10 <sup>-5</sup>	1
198	390	0.2954	2.696	2.01 . „	0.2412	3.635	2.32 . 10 <sup>-4</sup>	1
120	319	0.2982	2.647	2.25 . „	0.2622	3.263	5.46 . „	
20	...	0.3107	2.375	4.20 . „	0.3010	2.598	2.52 . 10 <sup>-3</sup>	0.96
15	...	0.3344	2.020	9.55 . „	0.3303	2.091	8.11 . „	0.93
12	...	0.3683	1.433	3.69 . 10 <sup>-2</sup>	0.3667	1.460	3.47 . 10 <sup>-2</sup>	0.85
11	...	0.4030	0.8313	1.48 . 10 <sup>-1</sup>	0.4028	0.835	1.46 . 10 <sup>-1</sup>	0.78

TABLE IV.

P.	P <sub>cal.</sub>	E <sub>i</sub> .	pa <sub>1</sub> .	a <sub>1</sub> .	E <sub>0</sub> .	pa <sub>2</sub> .	a <sub>2</sub> .	f.	E <sub>i</sub> - E <sub>0</sub>
620	4100	0.3458	1.923	1.50 . 10 <sup>-2</sup>	0.2161	4.069	8.53 . 10 <sup>-5</sup>	1	0.1297
350	4910	0.3507	1.738	1.83 . „	0.2555	3.309	4.91 . 10 <sup>-4</sup>	1	0.0952
272	3970	0.3463	1.814	1.54 . „	0.2767	3.030	9.33 . „	1	0.0696
72	...	0.3490	1.767	1.71 . „	0.3081	2.475	3.55 . 10 <sup>-3</sup>	0.95	0.0409
38	...	0.3578	1.615	2.43 . „	0.3378	1.961	1.09 . 10 <sup>-3</sup>	0.91	0.0200
37	...	0.3718	1.372	4.25 . „	0.3642	1.504	3.13 . „	0.86	0.0076
35	...	0.4104	0.703	1.98 . 10 <sup>-1</sup>	0.4090	0.7276	1.87 . 10 <sup>-1</sup>	0.78	0.0014
36	...	0.3788	1.251	5.61 . 10 <sup>-2</sup>	0.3727	1.357	4.40 . 10 <sup>-3</sup>	0.84	0.0061

(0.10-0.20.)

$E_i - E_c$	$a_1/a_2$	$a_2/a_1$	$[H_1]$	$[Cl_1]$	$[H_2]$	$z$	$z/S$
0.0800	24.3	0.04	$1.36 \cdot 10^{-3}$	$2.29 \cdot 10^{-6}$	$5.58 \cdot 10^{-5}$	$1.36 \cdot 10^{-3}$	$0.92 \cdot 10^{-4}$
0.0387	4.68	0.21	1.48 . .	$0.68 \cdot 10^{-4}$	$3.17 \cdot 10^{-4}$	1.41 . .	0.96 . .
0.0170	1.97	0.51	2.65 . .	6.90 . .	$1.34 \cdot 10^{-3}$	1.96 . .	1.33 . .
0.0043	1.19	0.84	8.63 . .	$6.11 \cdot 10^{-3}$	7.25 . .	2.55 . .	1.73 . .

(0.20-0.30.)

$E_i - E_c$	$a_1/a_2$	$a_2/a_1$	$[H_1]$	$[Cl_1]$	$[H_2]$	$z$	$z/S$
0.0900	36.2	0.03	$1.61 \cdot 10^{-3}$	$1.22 \cdot 10^{-6}$	$4.44 \cdot 10^{-5}$	$1.61 \cdot 10^{-3}$	$2.01 \cdot 10^{-4}$
0.0542	8.69	0.12	2.01 . .	$2.68 \cdot 10^{-5}$	$2.32 \cdot 10^{-4}$	1.98 . .	2.48 . .
0.0360	4.13	0.24	2.25 . .	$1.33 \cdot 10^{-4}$	5.46 . .	2.12 . .	2.66 . .
0.0097	1.67	0.60	4.38 . .	$1.57 \cdot 10^{-3}$	$2.63 \cdot 10^{-3}$	2.81 . .	3.52 . .
0.0041	1.18	0.85	$1.03 \cdot 10^{-2}$	7.43 . .	8.74 . .	2.88 . .	3.62 . .
0.0016	1.06	0.94	4.35 . .	$3.86 \cdot 10^{-2}$	$4.08 \cdot 10^{-2}$	4.90 . .	6.14 . .
0.0002	1.01	0.99	$1.90 \cdot 10^{-1}$	$1.86 \cdot 10^{-1}$	$1.85 \cdot 10^{-1}$	3.70 . .	4.55 . .

(0.30-0.40.)

$E_m$	$a_1/a_2$	$a_2/a_1$	$[H_1]$	$[Cl_1]$	$[H_2]$	$z$	$z/S$
0.1298	176	0.006	$1.50 \cdot 10^{-2}$	$5 \cdot 10^{-6}$	$8.53 \cdot 10^{-5}$	$1.50 \cdot 10^{-2}$	$5.15 \cdot 10^{-4}$
0.0922	37.2	0.03	1.83 . .	$1.3 \cdot 10^{-5}$	$4.91 \cdot 10^{-4}$	1.83 . .	6.30 . .
0.0702	16.4	0.06	1.54 . .	5.7 . .	9.33 . .	1.54 . .	5.28 . .
...	5.11	0.20	1.80 . .	$0.7 \cdot 10^{-2}$	$3.74 \cdot 10^{-3}$	1.73 . .	5.93 . .
...	2.22	0.45	2.67 . .	5.4 . .	$1.20 \cdot 10^{-2}$	2.13 . .	7.30 . .
...	1.36	0.74	4.95 . .	$2.68 \cdot 10^{-2}$	3.62 . .	2.25 . .	7.75 . .
...	1.06	0.94	$2.54 \cdot 10^{-1}$	$2.26 \cdot 10^{-1}$	$2.40 \cdot 10^{-1}$	2.89 . .	9.94 . .
...	1.28	0.78	$6.69 \cdot 10^{-2}$	$4.07 \cdot 10^{-2}$	$5.24 \cdot 10^{-2}$	2.62 . .	8.98 . .

P.	P	$E_i$	$pa_1$	$a_1$	$E_0$	$pa_2$	$a_2$	$f$	$E_i - E_0$	$E_m$
905	5220	0.3548	1.667	$2.15 \cdot 10^{-2}$	0.2375	3.700	$2.00 \cdot 10^{-4}$	1	0.1173	0.1173
640	5500	0.3555	1.654	2.22 . „	0.2703	3.130	7.41 . „	1	0.0852	...
383	5450	0.3548	1.667	2.15 . „	0.2940	2.720	$1.91 \cdot 10^{-3}$	0.98	0.0608	0.0605
154	...	0.3560	1.646	2.26 . „	0.3143	2.268	4.29 . „	0.95	0.0414	...
71	...	0.3626	1.531	2.94 . „	0.3410	1.905	$1.25 \cdot 10^{-2}$	0.90	0.0216	0.0220
43	...	0.3778	1.268	5.40 . „	0.3697	1.408	3.91 . „	0.85	0.0081	0.0085
38	...	0.3981	0.916	$1.21 \cdot 10^{-1}$	0.3948	0.974	$1.06 \cdot 10^{-1}$	0.80	0.0032	...
35	...	0.4265	0.424	3.77 . „	0.4255	0.442	3.62 . „	0.76	0.0010	0.0007
42	...	0.3838	1.164	$6.86 \cdot 10^{-2}$	0.3775	1.273	$5.33 \cdot 10^{-2}$	0.83	0.0063	...

TABLE VI. (Loe

$$z_1 = \frac{a_2}{f} \left[ \frac{a_2}{a_1} - \frac{a_1}{a_2} \right]$$

$pa_1 =$ “ $p_H$ inside.”	$pa_2 =$ “ $p_H$ outside.”	$pa_1 - pa_2$	$a_1$	$a_2$	$f$	$a_2/a_1$	$a_1/a_2$
4.56	4.14	0.42	$2.75 \cdot 10^{-5}$	$7.24 \cdot 10^{-5}$	1	2.63	0.38
4.31	3.78	0.53	4.90 . „	$1.66 \cdot 10^{-4}$	1	3.39	0.30
4.03	3.44	0.59	9.33 . „	3.63 . „	1	3.89	0.26
3.85	3.26	0.59	$1.41 \cdot 10^{-4}$	5.50 . „	0.99	3.89	0.26
3.33	2.87	0.46	4.68 . „	$1.35 \cdot 10^{-3}$	0.98	2.88	0.34
3.25	2.81	0.44	5.62 . „	1.55 . „	0.97	2.75	0.35
2.85	2.53	0.32	$1.41 \cdot 10^{-3}$	2.95 . „	0.96	2.09	0.48
2.52	2.28	0.24	3.02 . „	5.25 . „	0.94	1.74	0.58
2.13	2.00	0.13	7.41 . „	$1.00 \cdot 10^{-2}$	0.92	1.35	0.74
1.99	1.89	0.10	$1.02 \cdot 10^{-2}$	1.29 . „	0.90	1.26	0.79
1.79	1.72	0.07	1.62 . „	1.86 . „	0.88	1.17	0.85
1.57	1.53	0.04	2.68 . „	2.96 . „	0.86	1.10	0.90

(0.40- .)

$a_1/a_2$	$a_2/a_1$	$[H_1]$	$[Cl_1]$	$[H_2]$	$z$	$z/S$	$z_a$
108	0.009	$2.15 \cdot 10^{-2}$	$2.0 \cdot 10^{-6}$	$2.0 \cdot 10^{-4}$	$2.15 \cdot 10^{-2}$	$6.28 \cdot 10^{-4}$	...
29.9	0.03	2.22. "	$2.5 \cdot 10^{-5}$	7.41. "	2.22. "	6.50. "	$2.15 \cdot 10^{-3}$
11.3	0.09	2.20. "	$1.7 \cdot 10^{-4}$	$1.95 \cdot 10^{-3}$	2.20. "	6.45. "	2.17. "
5.27	0.19	2.38. "	$0.09 \cdot 10^{-2}$	4.52. "	2.29. "	6.70. "	2.27. "
2.35	0.42	3.27. "	0.60. "	$1.39 \cdot 10^{-2}$	2.68. "	7.85. "	2.67. "
1.38	0.72	6.36. "	3.33. "	4.60. "	3.03. "	8.85. "	3.21. "
1.14	0.88	$1.51 \cdot 10^{-1}$	$1.16 \cdot 10^{-1}$	$1.33 \cdot 10^{-1}$	3.56. "	10.10. "	3.40. "
1.04	0.96	4.96. "	4.58. "	4.76. "	3.82. "	11.15. "	3.48. "
1.29	0.78	$8.28 \cdot 10^{-2}$	$5.00 \cdot 10^{-2}$	$6.42 \cdot 10^{-2}$	3.28. "	9.59. "	3.29. "

Proteins, etc., p. 128, table xi.)

$$z_2 = \frac{14.6 \cdot a_1/f}{1 + 2100 \cdot a_1/f}$$

$a_1/f$	$a_2/f$	$z_1$	$a_1/fz_1$	$z_2$	$z_2 - z_1$
$2.75 \cdot 10^{-3}$	$7.24 \cdot 10^{-5}$	$0.16 \cdot 10^{-3}$	$1.72 \cdot 10^{-1}$	$0.26 \cdot 10^{-3}$	$+0.10 \cdot 10^{-3}$
4.90. "	$1.66 \cdot 10^{-4}$	0.51. "	$9.6 \cdot 10^{-2}$	0.65. "	+0.14. "
9.33. "	3.63. "	1.32. "	7.1. "	1.30. "	-0.02. "
$1.43 \cdot 10^{-4}$	5.55. "	2.00. "	7.0. "	1.61. "	-0.39. "
4.80. "	$1.38 \cdot 10^{-3}$	3.50. "	$1.37 \cdot 10^{-1}$	3.50. "	...
5.85. "	1.60. "	3.84. "	1.52. "	3.86. "	+0.02. "
$1.47 \cdot 10^{-3}$	3.07. "	4.95. "	2.97. "	5.25. "	+0.30. "
3.22. "	5.59. "	6.48. "	4.96. "	6.10. "	-0.38. "
8.15. "	$1.09 \cdot 10^{-2}$	6.63. "	1.23	6.60. "	-0.03. "
$1.12 \cdot 10^{-3}$	1.44. "	6.77. "	1.66	6.70. "	-0.07. "
1.81. "	2.12. "	6.80. "	2.66	6.80. "	...
3.13. "	3.45. "	6.90. "	4.55	6.86. "	-0.05. "

$z/S$  is plotted against  $p_{a_2}$ . As the figure shows, the quantity of adsorbed ions is fairly constant when the acidity outside the membrane is low, and rises when the acidity increases. A qualitative analysis of the dialysed sulphur sol gave no reaction for chlorine. The ions adsorbed in such a sol may therefore be those of some other acid, and the concentration of this is :

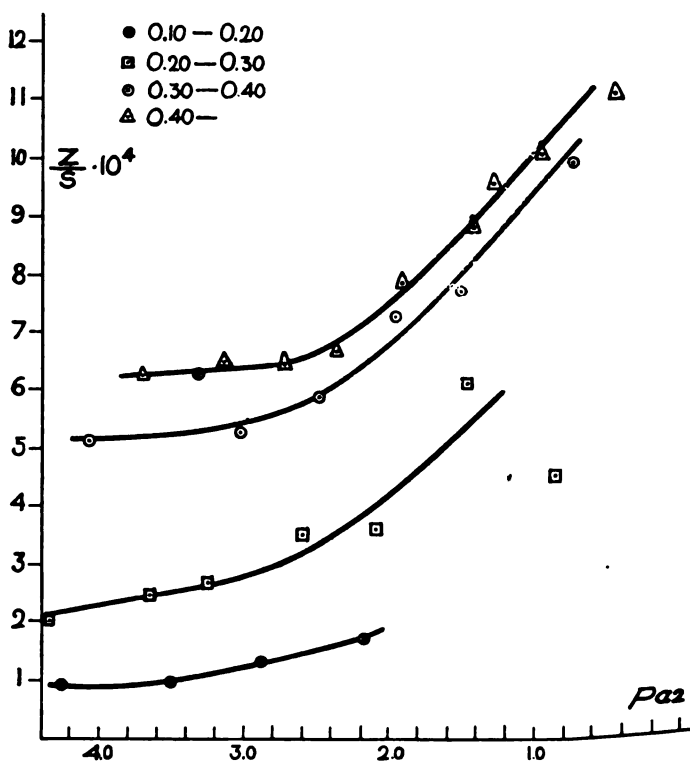
0.09 millimol per gram sulphur for the sol 0.10-0.20

0.2 " " " " " " " 0.20-0.30

0.5 " " " " " " " 0.30-0.40

0.6 " " " " " " " 0.40-

Fig. 3.



From their investigations, Freundlich and Scholtz \* have drawn the conclusion that the stability of the sulphur sols depends upon adsorbed pentathionic acid, and that the

\* *L. c.*

quantity of adsorbed acid in a Raffo sol is 0.47–0.69 millimol per gram sulphur. My experiments confirm such an assumption.

When, however, the hydrochloric acid concentration rises, chlorine ions become adsorbed. Langmuir has in some of his papers suggested a theory of adsorption\*. Gustaver† has successfully used this theory in investigating the adsorption of picric acid by charcoal. Langmuir assumes in his theory that on the surface of the adsorbing substance there are a certain number of elementary spaces, where there are residual valencies. If Langmuir's theory is applicable to the adsorption of ions on colloidal particles, we may write

$$z = \frac{k_1 c}{1 + k_2 c}, \quad \dots \quad (14)$$

where  $z$  is the concentration of adsorbed ions,  $c$  the concentration of the same ions in the solution, and  $k_1$  and  $k_2$  are constants. I have tried to apply this formula to the results reproduced in Table V. The adsorbed ions are partly chlorine ions and partly ions of another acid, possibly pentathionic acid; and if the concentration of this is equal to  $z$  in the first experiment in Table V. ( $= 2.15 \cdot 10^{-2}$ ), the other values of  $z$  may be expressed by:

$$z_a = 2.15 \cdot 10^{-2} + \frac{1.5 \text{ Cl}_1}{1 + 111 \text{ Cl}_1} \quad \dots \quad (15)$$

The results obtained by calculating according to this formula are reproduced in column  $z_a$ , Table V. The agreement between  $z$  and  $z_a$  is fairly good.

As an analysis shows, there are also neutral HCl molecules adsorbed on the sulphur particles. I have, however, not determined their amount, as it was of little importance for this research, and as the time I had at my disposal was very short. I will at least point out that I have in my experiments been rather far from the point of reversible coagulation. For instance, in Table V. I have not been able to measure the adsorption of ions beyond an acidity of 0.5 N, and for this sol the reversible coagulation sets in at an acidity of about 5 N. This method gives therefore no information concerning the variation in ionic adsorption when the acidity varies between 0.5 and 5 normal.

\* I. Langmuir, Journ. Amer. Chem. Soc. xxxviii. (1916); xxxix. (1917); xl. (1917).

† B. Gustaver, *Kolloidchem. Beih.* xv. (1922).

J. Loeb has, in his monograph "Proteins and the Theory of Colloidal Behaviour," given an account of his experiments on gelatine. He thinks he has proved that gelatine gives a real chemical reaction with acids or bases. His point of view can doubtless be best expressed by his own words, taken from the preface of his book:—

"Colloid Chemistry has been developed on the assumption that the ultimate unit in colloidal solutions is not the isolated molecule or ion but an aggregate of molecules or ions, the so-called micella of Naegeli. Since it seemed improbable that aggregates could combine in stoichiometrical proportions with acids, alkalies, or salts, the conclusion was drawn that electrolytes were adsorbed on the surface of colloidal particles according to a purely empirical formula, Freundlich's adsorption formula. The writer's investigations have led to the result that this last conclusion is based on a methodical error, as far as the proteins are concerned. . . . It is found that proteins combine with acids and alkalies according to the stoichiometrical laws of the classical chemistry and that the chemistry of proteins does not differ from the chemistry of crystalloids."

Loeb has, among other things, measured the membrane potential and the osmotic pressure, and the curves obtained when the membrane potential and the osmotic pressure are plotted against the values of  $p_H$  are of a different type from those I have obtained for colloidal sulphur. By adding HCl to gelatine and starting from the isoelectric point, the E.M.F. and O.P. increase, pass through a maximum, and then decrease. It may be of some interest to see how the concentration of the nondialysable ions varies with the acidity. It is possible to calculate this for HCl according to formula (7). For  $H_2SO_4$ ,  $H_3PO_4$ , etc., this formula is not applicable, because the approximations made in its deduction are not allowable for these acids. The experimental values are taken from Loeb's monograph, p. 128, table xi., and reproduced in Table VI. in this paper. In this table  $p_{a_1}$  and  $p_{a_2}$  are written instead of Loeb's values, " $p_H$  inside" and " $p_H$  outside." The other letters in the table have the same meaning as in the preceding tables in this paper.

I have, however, tried to apply Langmuir's adsorption theory to the case of gelatine by making a theoretical calculation of the  $z$  values. In this case there would be an adsorption of hydrogen ions, and the adsorption formula would be

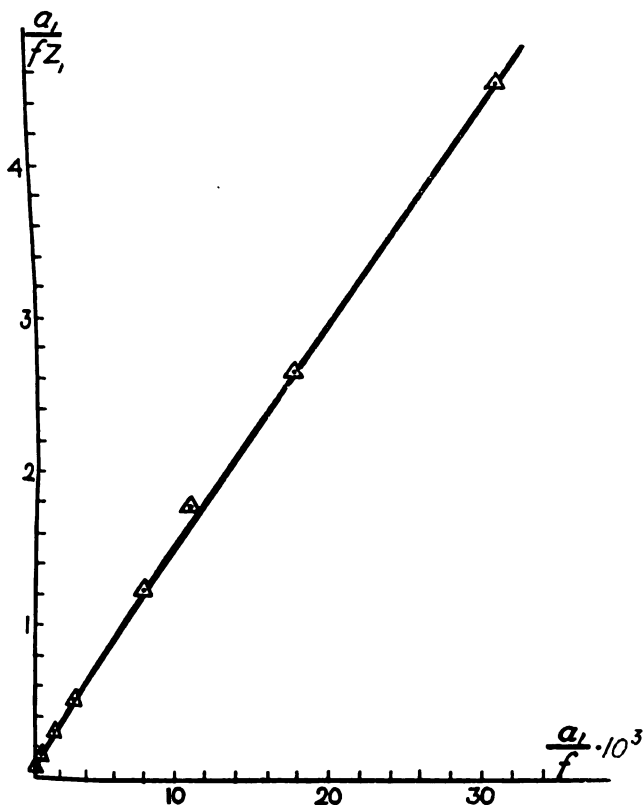
$$z = \frac{k_1 a_1 / f}{1 + k_2 a_1 / f}, \quad \cdot \cdot \cdot \cdot \cdot \quad (16)$$

or transformed,

$$\frac{a_1}{fz} = \frac{k_2}{k_1} \frac{a_1}{f} + \frac{1}{k_1} \dots \dots \dots (17)$$

If  $a_1/fz$  is plotted against  $a_1/f$  it is obvious from equation (17) that all the points would lie on a straight line if Langmuir's adsorption formula were applicable. This is done in fig. 4,

Fig. 4.



and, as the figure shows, this is the case. If the constants  $k_1$  and  $k_2$  are calculated from this straight line, the formula (16) can be written :

$$z_2 = \frac{14.6 \cdot a_1/f}{1 + 2100 a_1/f} \dots \dots \dots (18)$$

From the columns  $z_2$  and  $z_2 - z_1$  in Table VI. it is evident



that the theoretical values for the amount of adsorbed ions and the values calculated from determinations of the activities inside and outside the membrane check surprisingly well, and it is therefore very likely that the "reaction" between gelatine and HCl is not a chemical reaction in the sense assumed by Loeb, but an adsorption process, and that the hydrogen ions are bound by means of residual valencies to the gelatine particles. Exceptions from this may occur in the region of the isoelectric point, where a real chemical reaction may take place. Besides this adsorption of hydrogen ions there is also an adsorption of neutral HCl molecules, as can be calculated from Loeb's experimental results. A closer criticism of Loeb's work is, however, outside the scope of this paper.

In a recent paper (*Zeitschrift für Physikalische Chemie*, cx. p. 656, 1924) N. Bjerrum has published a research entitled: "Zur Theorie der osmotischen Drucke, der Membranpotentiale und der Ausflockung von Kolloiden." In this paper he has shown that colloidal chromium hydroxide gives a membrane equilibrium effect. He supposes that this is due to the fact that colloidal chromium hydroxide is to be considered as a high molecular, multivalent, strong electrolyte. Unfortunately there are in this paper a number of errors, and I will here call attention to only a few of them.

The particles in the colloid are positively charged,  $q$  is the average number of positive charges per chromium atom,  $[\text{Cr}]$  the number of chromium atoms per litre,  $p$  the amount of adsorbed anions per chromium atom, and on p. 677 he writes: "Fügt man zu  $p$ , die Zahl der adsorbierten Anionen,  $q$ , die Zahl der freien Ladungen, so erhält man die Gesamtladung der Kolloidpartikeln pro Chromatom." In table 8 (p. 676) is a column with the sum (not algebraical) of  $p + q$ . A sum of positive and negative charges cannot, however, be an expression for the charge of colloidal particles. Upon closer consideration of Bjerrum's experimental results, one finds that  $p$  is about 10 times as large as  $q$ . According to this the particle would be negatively charged, a conclusion which is opposed to his experimental results. From his method of determining  $p$  it is, however, evident that  $p$  is the quantity of adsorbed chromium chloride or hydrochloric acid molecules.  $q[\text{Cr}]$  signifies the quantity designated by  $z$  in the preceding part of this paper, and is therefore the concentration of adsorbed cations (chromium ions?).

Bjerrum supposes further that  $q$  is a constant. As he has not kept the chromium concentration constant it is impossible, according to equation (7), to calculate  $q$  values which can be

compared with each other. In Bjerrum's paper, p. 663, table 1, three experiments made the 28th October, the 5th November, and the 20th November, 1919, are, however, described, where the chromium concentration is constant ( $[Cr]=0.051$ ) and the acidity varies. The results are assembled in Table VII.

TABLE VII.

$a_2/f.$	$E_m.$	$a_2/a_1.$	$a_1/a_2.$	$x=q[Cr].$	$q.$
0.005	0.0091	1.44	0.70	0.0037	0.073
0.0025	0.0161	1.90	0.53	0.0034	0.067
0.001	0.0282	3.08	0.32	0.0028	0.055

From this table it is obvious that the amount of adsorbed cations increases with the acidity and  $q$  is not to be considered as a constant. All the conclusions which Bjerrum has drawn from this assumption—for instance, that the number of chromium atoms per chromium hydroxide particle is 1000, etc.—must therefore be wrong. On p. 672, table 6, Bjerrum has calculated the values of  $q$ , but these are only about half as large as those given in Table VII. I think that this depends, among other things, upon the fact that Bjerrum has used the osmotic pressure for the calculation of  $q$ , which is not permissible for these large particles according to Hammarsten's and this research. In closing, I will only correct a mathematical error. In Bjerrum's paper

$$x = \frac{E_m F}{RT} \quad \text{and} \quad P_2 = RT cx^2 \quad (\text{formula 13}).$$

The formula (22) should therefore be

$$P_2 = \frac{F^2}{RT} E_m^2 c,$$

and thus formula (23)

$$E_m = \text{const.} \sqrt{\frac{P_2}{c}}$$

instead of Bjerrum's formula. I have not calculated the constant as the formula is of very little importance, partly because, as already stated, the osmotic pressure cannot be

used for such calculations, and partly because the cases where the series development can be broken off at the first term, as Bjerrum has done, should be considered as exceptions.

The present investigation was carried out with the assistance of a stipendium from C. F. Liljewalch's Stipendium Fund of the University of Upsala.

I desire to take this opportunity of expressing my indebtedness to Prof. F. G. Donnan for his kindly interest and helpful criticism. I also wish to thank Prof. A. V. Hill for his kindness in allowing me to use one of his centrifuges.

The Sir William Ramsay Laboratories of  
Inorganic and Physical Chemistry,  
University College, London.  
November 1924.

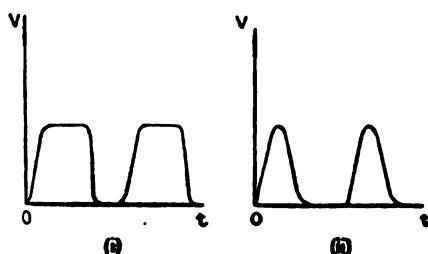
IV. *The Distribution of Energy in the Continuous X-ray Spectrum.* By MAURICE H. BELZ, M.Sc., Lecturer in Mathematics in the University of Melbourne\*.

THE accurate knowledge of the distribution of the energy emitted from an X-ray bulb under any given form of potential and current is of signal importance in all applications of the rays. If it were possible simply and quickly to predict the nature of the distribution of the energy from a knowledge of the variations of potential and current, it might be anticipated that a standardization of methods would be possible, especially in regard to applications to therapy. It is now well known that an X-ray tube, for example a standard Coolidge tube, will emit rays of different quality depending on the form of the applied potential. If a comparison be made between the energy wave-length curves for different types of voltage, it is found that for equality of maximum potential and mean current the curves are considerably different. The maximum energy is emitted for different wave-lengths, and the measure of this maximum energy is different for each case. This fact seems not only to rob the modern practice of deep therapy X-ray treatment of a scientific basis, but also to give to it a suggestion of chance. In particular, the treatment for a certain disease may be expressed as a dose of a certain potential and a certain

\* Communicated by Prof. T. H. Laby, M.A., Sc.D., F.Inst.P.

current acting for a specified time. This time is governed in the first place by the erythema dose, and the treatment may be thus expressed as equivalent to a certain number of such doses either simultaneously through several ports of entry or repeatedly through one port, sufficient time being allowed to elapse between doses to prevent the occurrence of an erythema. However, this treatment will be different for each machine used. The erythema dose is not only a function of the applied maximum potential and the current through the tube, but most particularly a function of the forms of the potential and current waves. The erythema dose thus depends entirely on the manner of the distribution, with wave-length, of the energy radiated from the tube. In the case of a Coolidge tube, where during the application of the potential the current may be regarded as approximately constant\*, if we compare the radiation produced by a potential wave of the form (i), fig. 1, with that produced by a potential wave of the form (ii), then allowing equivalence

Fig. 1.



of maximum potential, current, and frequency, we can assert that the radiation in the first case will have a maximum energy for a shorter wave-length than in the second case, and, further, that the value of this maximum will be greater in the first case than in the second. Thus the erythema dose may be altogether different in the two cases, and consequently there can be no uniformity of treatment. If, however, X-ray therapy is based on the physical characteristics of the radiation, that is to say, if the dose is expressed in terms of a maximum energy at a given wave-length acting for a given time, a real standardization of treatment may be hoped for. - The practitioner would then

\* The oscillograph records of the current wave obtained by Crowther (Camb. Phil. Soc. Proc. xxii. p. 70, 1924) in the case of a transformer justify this approximation.

only require to fulfil these conditions for successful treatment, and successful treatment of diseases for which deep therapy is prescribed must be a distinct step forward. Recent improvements in the physical basis of X-ray treatment have been rewarded to such an extent by better results as to encourage further efforts.

The only direct procedure to determine the energy distribution in the radiation from an X-ray bulb is by the employment of an X-ray spectrometer. To conduct such a determination is not only a tedious and difficult task for a medical man, but in most cases would be quite impossible owing to limitations of time and space. It is the object of this paper to point a way to the determination of the energy distribution curve, having given the oscillograph form of the applied potential. The necessary observations upon which any theory may be based are only available for a standard Coolidge X-ray tube, and this tube is the one most commonly employed in applications of X-rays. It will be shown that other types of tubes may be similarly considered, provided that sufficient is known experimentally of their performances.

The commencement of any such determination of the energy wave-length distribution must be made by considering the radiation emitted from the tube when the electrons all have the same speed, that is by considering the case of a constant potential. We may then proceed in two ways. First, we may examine theoretically the relation of the change of kinetic energy of the electron to energy of radiation. Any such treatment involves a number of assumptions, and consequently may be expected to be only an approximation. Theoretical calculations have been made by March\*, Davis†, Brillouin‡, Behukén§ and others, but Kirkpatrick|| has shown that the theoretical curves only fit the experimental curves very roughly, and accordingly cannot be used as a basis for prediction.

The second method of procedure will thus be from a study of the observed curves for different constant voltages, which have been made to represent the energy distribution of the radiation emitted from the anticathode by the application of a number of corrections. While many observers have examined the distribution from a Coolidge tube with a

\* March, *Phys. Zeit.* xxii. pp. 209, 429 (1921).

† Davis, *Phys. Rev.* ix. p. 64 (1917).

‡ Brillouin, *Comptes Rendus*, clxx. p. 274 (1920).

§ *Zeit. f. Techn. Physik*, vii. p. 153 (1921); and *Zeit. f. Physik*, Bd. iv. p. 241 (1921).

|| Kirkpatrick, *Phys. Rev.* xxii. p. 37 (1923).

tungsten anticathode, it is a matter for regret that only two\* have carried out these corrections, and as the results of these two observers are not the same, a definite conclusion cannot be arrived at from a study of their curves. The first systematic attempt to coordinate the observations from a Coolidge tube was made by Dauvillier†, who found that under different constant voltages and currents the energy distribution curves satisfied certain definite conditions. While Kirkpatrick‡ disagrees with one of these conditions, he makes no attempt at definiteness and does not examine any of the other conditions. For this reason Dauvillier's curves have been chosen as a basis for calculation.

### Dauvillier's Experimental Curves.

The principal deductions made by Dauvillier from his curves are as follows :—

(i.) Corresponding to any given voltage  $V$ , the shortest wave-length at which energy is radiated is given by the relation

$$\lambda_0 = \frac{ch}{eV},$$

where  $c$  is the velocity of light,  $3 \times 10^{10}$  cm./sec.,  $h$  is Planck's constant,  $6.555 \times 10^{-27}$  ergs, and  $e$  is the charge on the electron,  $4.774 \times 10^{-10}$  e.s.u. If  $V$  is expressed in kilovolts, the shortest wave-length,  $\lambda_0$ , expressed in Ångström units, is given practically by the relation

$$\lambda_0 = \frac{12.348}{V}.$$

This relation had been proved experimentally by a number of independent observers §.

(ii.) The maximum energy is radiated at a wave-length  $\lambda_m$  given by

$$\lambda_m = 1.3 \lambda_0,$$

provided that  $\lambda_0$  is less than  $0.3 \text{ Å.U.}$  (p. 113) ||.

\* Dauvillier, *Ann. de Physique*, xiii. p. 49 (1920), and Kirkpatrick, *loc. cit.*

† Dauvillier, *loc. cit.*

‡ Kirkpatrick, *loc. cit.*

§ See de Broglie, *Les Rayons*, x. p. 77 (1922).

|| (p. 113) and similar references give the pages in Dauvillier's paper (*loc. cit.*) where the experimental information is recorded.

This law corresponds to Wien's displacement law for the radiation from a black body. For  $\lambda_0 > 0.3 \text{ Å.U.}$   $\lambda_m > 1.3 \lambda_0$ , giving for  $\lambda_0 = 0.4 \text{ Å.U.}$   $\lambda_m = 1.5 \lambda_0$  approximately.

(iii.) For equal currents through the tube, the maximum energy radiated for different constant potentials is proportional to the square of the potential (p. 115).

(iv.) For equal currents through the tube, the total energy radiated, that is, the area of the distribution curve, for different constant potentials is proportional to the square of the potential (p. 115).

(v.) For equal potentials and different currents through the tube, the minimum energy in each case is radiated at the wave-length given by  $\lambda_m = 1.3 \lambda_0$ , but the ordinates and areas of the curves are directly proportional to the intensities of the currents in each case (p. 120).

It is possible to find an empirical expression to represent the distribution curve. The conditions to be fulfilled by any such expression may, from Dauvillier's conclusions, be stated briefly thus:—

If  $E$  represents the energy radiated between the wave-lengths  $\lambda$  and  $\lambda + d\lambda$ , then

$$(i.) E = 0 \text{ for } \lambda = \lambda_0 = \frac{12.348}{V} \text{ Å.U.}$$

(ii.) The maximum energy  $E_m$  occurs at  $\lambda_m = 1.3 \lambda_0$ , if  $\lambda_0 < 0.3 \text{ Å.U.}$

(iii.)  $E_m = kV^2$ , where  $k$  is a constant, provided the current is constant.

(iv.) The area of the curve,  $A$ , is given by  $A = k'V^2$ , where  $k'$  is a constant, provided the current is constant.

(v.)  $E$ , the energy at any wave-length, and  $A$ , the area of the curve, are both proportional to  $i$ , where  $i$  is the current through the tube.

### *Empirical Law of Distribution.*

It is a simplification in the treatment to write  $x = \frac{\lambda - \lambda_0}{\lambda_0}$

and to consider the graphs wherein energy is plotted against  $x$ . The curves given by Dauvillier for voltages 71 kilovolt and 53.5 kilovolt and equal currents,  $0.5 \times 10^{-3}$  amp., have been redrawn to this new scale and are represented by the curves A and B, fig. 2. In this figure the scale of ordinates is arbitrary. If we denote energy by  $y$ .

then if  $y = f(x)$  is the empirical relation between  $y$  and  $x$ , we must have the following conditions :—

(i.)  $y = 0$  for  $x = 0$ .

(ii.)  $dy/dx = 0$  for  $x = h$ , where  $h = 0.3$ , giving a maximum value of  $y$ .

(iii.)  $y_{\max} = f(h) = kV^2$ .

(iv.)  $\int_0^x y \cdot dx = k_1 V^3$ .

(v.) The dependence of  $y$  on the current can be expressed by a further relation of the form  $y = i \cdot f(x)$ , where  $i$  is the current through the tube. If we can thus find the form of  $f(x)$  for any given current, the values of  $y$  for any other current can be found by multiplying by an appropriate factor. In the following, the experimental curves for a current 0.5 milliamp. have been employed as the basis of empirical calculations.

The analogy of the distribution curve for X-radiation to that for black body radiation suggested in the first place functions of the type governing the latter radiation. However, all such functions are ineffective on account of their failure to satisfy condition (i.) or difficulty in satisfying condition (iv.). It was thus decided to investigate some similar types of functions which would easily satisfy the conditions. A complete investigation was made of the function

$$y = (ax + bx^2 + cx^3) \cdot e^{-px},$$

which can be made to satisfy all the conditions. It was unfortunate that the constants of the curve, as determined by the conditions, gave two maxima and a minimum, whereas for slightly different values the curve only had one maximum.

Finally, the following function was examined and found to fit the experimental curves quite well.

We take

$$y = a(e^{-bx} - e^{-cx}).$$

This vanishes for  $x = 0$ .

Further,

$$dy/dx = a(-be^{-bx} + ce^{-cx})$$

and this has to vanish for  $x = h$ , giving

$$be^{-bh} - ce^{-ch} = 0.$$

For this value of  $x$  the maximum value of  $y$  is

$$y_m = a(e^{-bh} - e^{-ch}) = kV^2 = E_m, \text{ say,}$$

where  $E_m$  is the maximum arbitrary ordinate of any of the



TABLE V.

P.	P	$E_i$	$pa_1$	$a_1$	$E_0$	$pa_2$	$a_2$	$f$	$E_i - E_0$	$E_m$
905	5220	0.3548	1.667	$2.15 \cdot 10^{-2}$	0.2375	3.700	$2.00 \cdot 10^{-4}$	1	0.1173	0.1173
640	5500	0.3555	1.654	2.22 . .	0.2703	3.130	7.41 . .	1	0.0852	...
383	5450	0.3548	1.667	2.15 . .	0.2940	2.720	$1.91 \cdot 10^{-3}$	0.98	0.0608	0.0635
154	...	0.3560	1.646	2.26 . .	0.3143	2.368	4.29 . .	0.95	0.0414	...
71	...	0.3626	1.531	2.94 . .	0.3410	1.905	$1.25 \cdot 10^{-2}$	0.90	0.0216	0.0220
43	...	0.3778	1.268	5.40 . .	0.3697	1.408	3.91 . .	0.85	0.0081	0.0085
38	...	0.3981	0.916	$1.21 \cdot 10^{-1}$	0.3948	0.974	$1.06 \cdot 10^{-1}$	0.80	0.0032	...
35	...	0.4265	0.424	3.77 . .	0.4255	0.442	3.62 . .	0.76	0.0010	0.0007
42	...	0.3838	1.164	$6.86 \cdot 10^{-2}$	0.3775	1.273	$5.33 \cdot 10^{-2}$	0.83	0.0063	...

TABLE VI. (Loeb :

$$z_1 = \frac{a_2}{f} \left[ \frac{a_2}{a_1} - \frac{a_1}{a_2} \right] ;$$

$pa_1 =$ "p <sub>H</sub> inside."	$pa_2 =$ "p <sub>H</sub> outside."	$pa_1 - pa_2$	$a_1$	$a_2$	$f$	$a_2 \cdot a_1$	$a_1/a_2$
4.56	4.14	0.42	$2.75 \cdot 10^{-5}$	$7.24 \cdot 10^{-5}$	1	2.63	0.38
4.31	3.78	0.53	4.90 . .	$1.66 \cdot 10^{-4}$	1	3.39	0.30
4.03	3.44	0.59	9.38 . .	3.63 . .	1	3.89	0.26
3.85	3.26	0.59	$1.41 \cdot 10^{-4}$	5.50 . .	0.99	3.89	0.26
3.33	2.87	0.46	4.68 . .	$1.35 \cdot 10^{-3}$	0.98	2.88	0.34
3.25	2.81	0.44	5.62 . .	1.55 . .	0.97	2.75	0.35
2.85	2.53	0.32	$1.41 \cdot 10^{-3}$	2.95 . .	0.96	2.09	0.48
2.52	2.28	0.24	3.02 . .	5.25 . .	0.94	1.74	0.58
2.13	2.00	0.13	7.41 . .	$1.00 \cdot 10^{-2}$	0.92	1.35	0.74
1.99	1.89	0.10	$1.02 \cdot 10^{-2}$	1.29 . .	0.90	1.26	0.79
1.79	1.72	0.07	1.62 . .	1.86 . .	0.88	1.17	0.85
1.57	1.53	0.04	2.68 . .	2.96 . .	0.86	1.10	0.90

(0.40- .)

$a_1/a_2$	$a_2/a_1$	$[H_1]$	$[Cl_1]$	$[H_2]$	$z$	$z/S$	$z_s$
108	0.009	$2.15 \cdot 10^{-2}$	$2.0 \cdot 10^{-6}$	$2.0 \cdot 10^{-4}$	$2.15 \cdot 10^{-2}$	$6.28 \cdot 10^{-4}$	...
29.9	0.03	2.22. "	$2.5 \cdot 10^{-5}$	7.41. "	2.22. "	6.50. "	$2.15 \cdot 10^{-2}$
11.3	0.09	2.20. "	$1.7 \cdot 10^{-4}$	$1.95 \cdot 10^{-3}$	2.20. "	6.45. "	2.17. "
5.27	0.19	2.38. "	$0.09 \cdot 10^{-2}$	4.52. "	2.29. "	6.70. "	2.27. "
2.35	0.42	3.27. "	0.60. "	$1.39 \cdot 10^{-2}$	2.68. "	7.85. "	2.67. "
1.38	0.72	6.36. "	3.33. "	4.60. "	3.03. "	8.85. "	3.21. "
1.14	0.88	$1.51 \cdot 10^{-1}$	$1.16 \cdot 10^{-1}$	$1.33 \cdot 10^{-1}$	3.56. "	10.10. "	3.40. "
1.04	0.96	4.96. "	4.58. "	4.76. "	3.82. "	11.15. "	3.48. "
1.29	0.78	$8.28 \cdot 10^{-2}$	$5.00 \cdot 10^{-2}$	$6.42 \cdot 10^{-2}$	3.28. "	9.59. "	3.29. "

Proteins, etc., p. 128, table xi.)

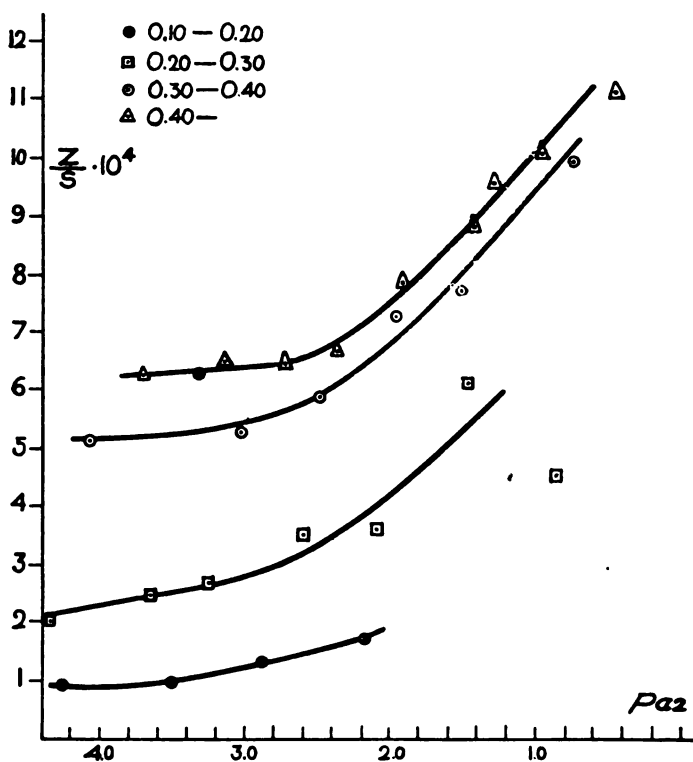
$$z_2 = \frac{14.6 \cdot a_1/f}{1 + 2100 \cdot a_1/f}$$

$a_1/f$	$a_2/f$	$z_1$	$a_1/fz_1$	$z_2$	$z_2 - z_1$
$2.75 \cdot 10^{-5}$	$7.24 \cdot 10^{-5}$	$0.16 \cdot 10^{-3}$	$1.72 \cdot 10^{-1}$	$0.26 \cdot 10^{-3}$	$+0.10 \cdot 10^{-3}$
4.90. "	$1.66 \cdot 10^{-4}$	0.51. "	$9.6 \cdot 10^{-2}$	0.65. "	+0.14. "
9.33. "	3.63. "	1.32. "	7.1. "	1.30. "	-0.02. "
$1.43 \cdot 10^{-4}$	5.55. "	2.00. "	7.0. "	1.61. "	-0.39. "
4.80. "	$1.38 \cdot 10^{-3}$	3.50. "	$1.37 \cdot 10^{-1}$	3.50. "	...
5.85. "	1.60. "	3.84. "	1.52. "	3.86. "	+0.02. "
$1.47 \cdot 10^{-3}$	3.07. "	4.95. "	2.97. "	5.25. "	+0.30. "
3.22. "	5.59. "	6.48. "	4.96. "	6.10. "	-0.38. "
8.15. "	$1.09 \cdot 10^{-2}$	6.63. "	1.23	6.60. "	-0.03. "
$1.12 \cdot 10^{-2}$	1.44. "	6.77. "	1.66	6.70. "	-0.07. "
1.81. "	2.12. "	6.90. "	2.66	6.80. "	...
3.13. "	3.45. "	6.90. "	4.55	6.86. "	-0.05. "

$z/S$  is plotted against  $p_{a_2}$ . As the figure shows, the quantity of adsorbed ions is fairly constant when the acidity outside the membrane is low, and rises when the acidity increases. A qualitative analysis of the dialysed sulphur sol gave no reaction for chlorine. The ions adsorbed in such a sol may therefore be those of some other acid, and the concentration of this is :

0.09 millimol per gram sulphur for the sol	0.10-0.20
0.2       "       "       "       "       "       "	0.20-0.30
0.5       "       "       "       "       "       "	0.30-0.40
0.6       "       "       "       "       "       "	0.40-

Fig. 3.



From their investigations, Freundlich and Scholtz\* have drawn the conclusion that the stability of the sulphur sols depends upon adsorbed pentathionic acid, and that the

\* *L. c.*

quantity of adsorbed acid in a Raffo sol is 0.47–0.69 millimol per gram sulphur. My experiments confirm such an assumption.

When, however, the hydrochloric acid concentration rises, chlorine ions become adsorbed. Langmuir has in some of his papers suggested a theory of adsorption\*. Gustaver† has successfully used this theory in investigating the adsorption of picric acid by charcoal. Langmuir assumes in his theory that on the surface of the adsorbing substance there are a certain number of elementary spaces, where there are residual valencies. If Langmuir's theory is applicable to the adsorption of ions on colloidal particles, we may write

$$z = \frac{k_1 c}{1 + k_2 c}, \quad \dots \quad (14)$$

where  $z$  is the concentration of adsorbed ions,  $c$  the concentration of the same ions in the solution, and  $k_1$  and  $k_2$  are constants. I have tried to apply this formula to the results reproduced in Table V. The adsorbed ions are partly chlorine ions and partly ions of another acid, possibly pentathionic acid; and if the concentration of this is equal to  $z$  in the first experiment in Table V. ( $= 2.15 \cdot 10^{-2}$ ), the other values of  $z$  may be expressed by:

$$z_a = 2.15 \cdot 10^{-2} + \frac{1.5 \text{ Cl}_1}{1 + 111 \text{ Cl}_1} \quad \dots \quad (15)$$

The results obtained by calculating according to this formula are reproduced in column  $z_a$ , Table V. The agreement between  $z$  and  $z_a$  is fairly good.

As an analysis shows, there are also neutral HCl molecules adsorbed on the sulphur particles. I have, however, not determined their amount, as it was of little importance for this research, and as the time I had at my disposal was very short. I will at least point out that I have in my experiments been rather far from the point of reversible coagulation. For instance, in Table V. I have not been able to measure the adsorption of ions beyond an acidity of 0.5 N, and for this sol the reversible coagulation sets in at an acidity of about 5 N. This method gives therefore no information concerning the variation in ionic adsorption when the acidity varies between 0.5 and 5 normal.

\* I. Langmuir, Journ. Amer. Chem. Soc. xxxviii. (1916); xxxix. (1917); xl. (1917).

† B. Gustaver, Kolloidchem. Beih. xv. (1922).

J. Loeb has, in his monograph "Proteins and the Theory of Colloidal Behaviour," given an account of his experiments on gelatine. He thinks he has proved that gelatine gives a real chemical reaction with acids or bases. His point of view can doubtless be best expressed by his own words, taken from the preface of his book :—

"Colloid Chemistry has been developed on the assumption that the ultimate unit in colloidal solutions is not the isolated molecule or ion but an aggregate of molecules or ions, the so-called micella of Naegeli. Since it seemed improbable that aggregates could combine in stoichiometrical proportions with acids, alkalies, or salts, the conclusion was drawn that electrolytes were adsorbed on the surface of colloidal particles according to a purely empirical formula, Freundlich's adsorption formula. The writer's investigations have led to the result that this last conclusion is based on a methodical error, as far as the proteins are concerned. . . . It is found that proteins combine with acids and alkalies according to the stoichiometrical laws of the classical chemistry and that the chemistry of proteins does not differ from the chemistry of crystalloids."

Loeb has, among other things, measured the membrane potential and the osmotic pressure, and the curves obtained when the membrane potential and the osmotic pressure are plotted against the values of  $p_H$  are of a different type from those I have obtained for colloidal sulphur. By adding HCl to gelatine and starting from the isoelectric point, the E.M.F. and O.P. increase, pass through a maximum, and then decrease. It may be of some interest to see how the concentration of the nondialysable ions varies with the acidity. It is possible to calculate this for HCl according to formula (7). For  $H_2SO_4$ ,  $H_3PO_4$ , etc., this formula is not applicable, because the approximations made in its deduction are not allowable for these acids. The experimental values are taken from Loeb's monograph, p. 128, table xi., and reproduced in Table VI. in this paper. In this table  $p_{a_1}$  and  $p_{a_2}$  are written instead of Loeb's values, " $p_H$  inside" and " $p_H$  outside." The other letters in the table have the same meaning as in the preceding tables in this paper.

I have, however, tried to apply Langmuir's adsorption theory to the case of gelatine by making a theoretical calculation of the  $z$  values. In this case there would be an adsorption of hydrogen ions, and the adsorption formula would be

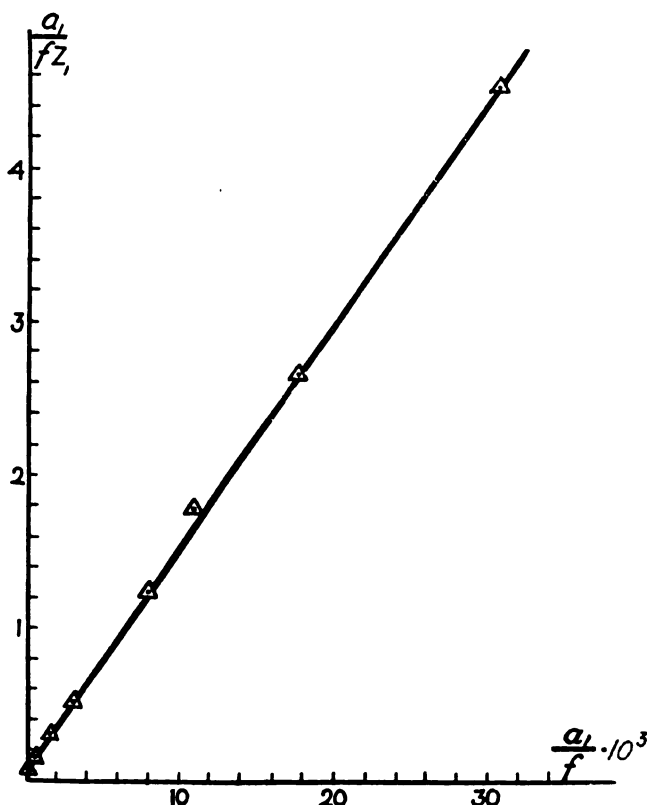
$$z = \frac{k_1 a_1 / f}{1 + k_2 a_1 / f}, \quad \cdot \cdot \cdot \cdot \cdot \quad (16)$$

or transformed,

$$\frac{a_1}{fz} = \frac{k_2}{k_1} \frac{a_1}{f} + \frac{1}{k_1} \dots \dots \dots (17)$$

If  $a_1/fz$  is plotted against  $a_1/f$  it is obvious from equation (17) that all the points would lie on a straight line if Langmuir's adsorption formula were applicable. This is done in fig. 4,

Fig. 4.



and, as the figure shows, this is the case. If the constants  $k_1$  and  $k_2$  are calculated from this straight line, the formula (16) can be written:

$$z_2 = \frac{14.6 \cdot a_1/f}{1 + 2100 a_1/f} \dots \dots \dots (18)$$

From the columns  $z_2$  and  $z_2 - z_1$  in Table VI. it is evident

that the theoretical values for the amount of adsorbed ions and the values calculated from determinations of the activities inside and outside the membrane check surprisingly well, and it is therefore very likely that the "reaction" between gelatine and HCl is not a chemical reaction in the sense assumed by Loeb, but an adsorption process, and that the hydrogen ions are bound by means of residual valencies to the gelatine particles. Exceptions from this may occur in the region of the isoelectric point, where a real chemical reaction may take place. Besides this adsorption of hydrogen ions there is also an adsorption of neutral HCl molecules, as can be calculated from Loeb's experimental results. A closer criticism of Loeb's work is, however, outside the scope of this paper.

In a recent paper (*Zeitschrift für Physikalische Chemie*, ex. p. 656, 1924) N. Bjerrum has published a research entitled: "Zur Theorie der osmotischen Drucke, der Membranpotentiale und der Ausflockung von Kolloiden." In this paper he has shown that colloidal chromium hydroxide gives a membrane equilibrium effect. He supposes that this is due to the fact that colloidal chromium hydroxide is to be considered as a high molecular, multivalent, strong electrolyte. Unfortunately there are in this paper a number of errors, and I will here call attention to only a few of them.

The particles in the colloid are positively charged,  $q$  is the average number of positive charges per chromium atom,  $[Cr]$  the number of chromium atoms per litre,  $p$  the amount of adsorbed anions per chromium atom, and on p. 677 he writes: "Fügt man zu  $p$ , die Zahl der adsorbierten Anionen,  $q$ , die Zahl der freien Ladungen, so erhält man die Gesamtladung der Kolloidpartikeln pro Chromatom." In table 8 (p. 676) is a column with the sum (not algebraical) of  $p + q$ . A sum of positive and negative charges cannot, however, be an expression for the charge of colloidal particles. Upon closer consideration of Bjerrum's experimental results, one finds that  $p$  is about 10 times as large as  $q$ . According to this the particle would be negatively charged, a conclusion which is opposed to his experimental results. From his method of determining  $p$  it is, however, evident that  $p$  is the quantity of adsorbed chromium chloride or hydrochloric acid molecules.  $q[Cr]$  signifies the quantity designated by  $z$  in the preceding part of this paper, and is therefore the concentration of adsorbed cations (chromium ions?).

Bjerrum supposes further that  $q$  is a constant. As he has not kept the chromium concentration constant it is impossible, according to equation (7), to calculate  $q$  values which can be

compared with each other. In Bjerrum's paper, p. 663, table 1, three experiments made the 28th October, the 5th November, and the 20th November, 1919, are, however, described, where the chromium concentration is constant ( $[\text{Cr}] = 0.051$ ) and the acidity varies. The results are assembled in Table VII.

TABLE VII.

$a_2/f.$	$E_m.$	$a_2/a_1.$	$a_1/a_2.$	$x=q[\text{Cr}].$	$q.$
0.005	0.0091	1.44	0.70	0.0037	0.073
0.0025	0.0161	1.90	0.53	0.0034	0.067
0.001	0.0282	3.08	0.32	0.0028	0.055

From this table it is obvious that the amount of adsorbed cations increases with the acidity and  $q$  is not to be considered as a constant. All the conclusions which Bjerrum has drawn from this assumption—for instance, that the number of chromium atoms per chromium hydroxide particle is 1000, etc.—must therefore be wrong. On p. 672, table 6, Bjerrum has calculated the values of  $q$ , but these are only about half as large as those given in Table VII. I think that this depends, among other things, upon the fact that Bjerrum has used the osmotic pressure for the calculation of  $q$ , which is not permissible for these large particles according to Hammarsten's and this research. In closing, I will only correct a mathematical error. In Bjerrum's paper

$$x = \frac{E_m F}{RT} \quad \text{and} \quad P_2 = RT c x^2 \quad (\text{formula 13}).$$

The formula (22) should therefore be

$$P_2 = \frac{F^2}{RT} E_m^2 c,$$

and thus formula (23)

$$E_m = \text{const.} \sqrt{\frac{P_2}{c}}$$

instead of Bjerrum's formula. I have not calculated the constant as the formula is of very little importance, partly because, as already stated, the osmotic pressure cannot be



used for such calculations, and partly because the cases where the series development can be broken off at the first term, as Bjerrum has done, should be considered as exceptions.

The present investigation was carried out with the assistance of a stipendium from C. F. Liljewaich's Stipendium Fund of the University of Upsala.

I desire to take this opportunity of expressing my indebtedness to Prof. F. G. Donnan for his kindly interest and helpful criticism. I also wish to thank Prof. A. V. Hill for his kindness in allowing me to use one of his centrifuges.

The Sir William Ramsay Laboratories of  
Inorganic and Physical Chemistry,  
University College, London.  
November 1924.

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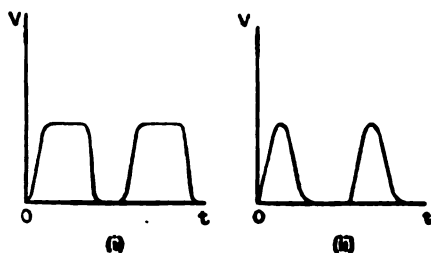
IV. *The Distribution of Energy in the Continuous X-ray Spectrum.* By MAURICE H. BELZ, M.Sc., Lecturer in Mathematics in the University of Melbourne\*.

THE accurate knowledge of the distribution of the energy emitted from an X-ray bulb under any given form of potential and current is of signal importance in all applications of the rays. If it were possible simply and quickly to predict the nature of the distribution of the energy from a knowledge of the variations of potential and current, it might be anticipated that a standardization of methods would be possible, especially in regard to applications to therapy. I is now well known that an X-ray tube, for example a standard Coolidge tube, will emit rays of different quality depending on the form of the applied potential. If a comparison be made between the energy wave-length curves for different types of voltage, it is found that for equality of maximum potential and mean current the curves are considerably different. The maximum energy is emitted for different wave-lengths, and the measure of this maximum energy is different for each case. This fact seems not only to rob the modern practice of deep therapy X-ray treatment of a scientific basis, but also to give to it a suggestion of chance. In particular, the treatment for a certain disease may be expressed as a dose of a certain potential and a certain

\* Communicated by Prof. T. H. Laby, M.A., Sc.D., F.Inst.P.

current acting for a specified time. This time is governed in the first place by the erythema dose, and the treatment may be thus expressed as equivalent to a certain number of such doses either simultaneously through several ports of entry or repeatedly through one port, sufficient time being allowed to elapse between doses to prevent the occurrence of an erythema. However, this treatment will be different for each machine used. The erythema dose is not only a function of the applied maximum potential and the current through the tube, but most particularly a function of the forms of the potential and current waves. The erythema dose thus depends entirely on the manner of the distribution, with wave-length, of the energy radiated from the tube. In the case of a Coolidge tube, where during the application of the potential the current may be regarded as approximately constant\*, if we compare the radiation produced by a potential wave of the form (i), fig. 1, with that produced by a potential wave of the form (ii), then allowing equivalence

Fig. 1.



of maximum potential, current, and frequency, we can assert that the radiation in the first case will have a maximum energy for a shorter wave-length than in the second case, and, further, that the value of this maximum will be greater in the first case than in the second. Thus the erythema dose may be altogether different in the two cases, and consequently there can be no uniformity of treatment. If, however, X-ray therapy is based on the physical characteristics of the radiation, that is to say, if the dose is expressed in terms of a maximum energy at a given wave-length acting for a given time, a real standardization of treatment may be hoped for. - The practitioner would then

\* The oscillograph records of the current wave obtained by Crowther (Camb. Phil. Soc. Proc. xxii. p. 70, 1924) in the case of a transformer justify this approximation.

only require to fulfil these conditions for successful treatment, and successful treatment of diseases for which deep therapy is prescribed must be a distinct step forward. Recent improvements in the physical basis of X-ray treatment have been rewarded to such an extent by better results as to encourage further efforts.

The only direct procedure to determine the energy distribution in the radiation from an X-ray bulb is by the employment of an X-ray spectrometer. To conduct such a determination is not only a tedious and difficult task for a medical man, but in most cases would be quite impossible owing to limitations of time and space. It is the object of this paper to point a way to the determination of the energy distribution curve, having given the oscillograph form of the applied potential. The necessary observations upon which any theory may be based are only available for a standard Coolidge X-ray tube, and this tube is the one most commonly employed in applications of X-rays. It will be shown that other types of tubes may be similarly considered, provided that sufficient is known experimentally of their performances.

The commencement of any such determination of the energy wave-length distribution must be made by considering the radiation emitted from the tube when the electrons all have the same speed, that is by considering the case of a constant potential. We may then proceed in two ways. First, we may examine theoretically the relation of the change of kinetic energy of the electron to energy of radiation. Any such treatment involves a number of assumptions, and consequently may be expected to be only an approximation. Theoretical calculations have been made by March\*, Davis†, Brillouin‡, Behruken§ and others, but Kirkpatrick|| has shown that the theoretical curves only fit the experimental curves very roughly, and accordingly cannot be used as a basis for prediction.

The second method of procedure will thus be from a study of the observed curves for different constant voltages, which have been made to represent the energy distribution of the radiation emitted from the anticathode by the application of a number of corrections. While many observers have examined the distribution from a Coolidge tube with a

\* March, *Phys. Zeit.* xxii. pp. 209, 429 (1921).

† Davis, *Phys. Rev.* ix. p. 64 (1917).

‡ Brillouin, *Comptes Rendus*, clxx. p. 274 (1920).

§ *Zeit. f. Techn. Physik*, vii. p. 153 (1921); and *Zeit. f. Physik*, Bd. iv. p. 241 (1921).

|| Kirkpatrick, *Phys. Rev.* xxii. p. 37 (1923).

tungsten anticathode, it is a matter for regret that only two\* have carried out these corrections, and as the results of these two observers are not the same, a definite conclusion cannot be arrived at from a study of their curves. The first systematic attempt to coordinate the observations from a Coolidge tube was made by Dauvillier†, who found that under different constant voltages and currents the energy distribution curves satisfied certain definite conditions. While Kirkpatrick‡ disagrees with one of these conditions, he makes no attempt at definiteness and does not examine any of the other conditions. For this reason Dauvillier's curves have been chosen as a basis for calculation.

### Dauvillier's Experimental Curves.

The principal deductions made by Dauvillier from his curves are as follows:—

(i.) Corresponding to any given voltage  $V$ , the shortest wave-length at which energy is radiated is given by the relation

$$\lambda_0 = \frac{ch}{eV},$$

where  $c$  is the velocity of light,  $3 \times 10^{10}$  cm./sec.,  $h$  is Planck's constant,  $6.555 \times 10^{-27}$  ergs, and  $e$  is the charge on the electron,  $4.774 \times 10^{-10}$  e.s.u. If  $V$  is expressed in kilovolts, the shortest wave-length,  $\lambda_0$ , expressed in Ångström units, is given practically by the relation

$$\lambda_0 = \frac{12.348}{V}.$$

This relation had been proved experimentally by a number of independent observers§.

(ii.) The maximum energy is radiated at a wave-length  $\lambda_m$  given by

$$\lambda_m = 1.3 \lambda_0,$$

provided that  $\lambda_0$  is less than  $0.3 \text{ Å.U.}$  (p. 113) ||.

\* Dauvillier, *Ann. de Physique*, xiii. p. 49 (1920), and Kirkpatrick, *loc. cit.*

† Dauvillier, *loc. cit.*

‡ Kirkpatrick, *loc. cit.*

§ See de Broglie, *Les Rayons*, x. p. 77 (1922).

|| (p. 113) and similar references give the pages in Dauvillier's paper (*loc. cit.*) where the experimental information is recorded.

This law corresponds to Wien's displacement law for the radiation from a black body. For  $\lambda_0 > 0.3 \text{ Å.U.}$   $\lambda_m > 1.3 \lambda_0$ , giving for  $\lambda_0 = 0.4 \text{ Å.U.}$   $\lambda_m = 1.5 \lambda_0$  approximately.

(iii.) For equal currents through the tube, the maximum energy radiated for different constant potentials is proportional to the square of the potential (p. 115).

(iv.) For equal currents through the tube, the total energy radiated, that is, the area of the distribution curve, for different constant potentials is proportional to the square of the potential (p. 115).

(v.) For equal potentials and different currents through the tube, the minimum energy in each case is radiated at the wave-length given by  $\lambda_m = 1.3 \lambda_0$ , but the ordinates and areas of the curves are directly proportional to the intensities of the currents in each case (p. 120).

It is possible to find an empirical expression to represent the distribution curve. The conditions to be fulfilled by any such expression may, from Dauvillier's conclusions, be stated briefly thus:—

If  $E$  represents the energy radiated between the wave-lengths  $\lambda$  and  $\lambda + d\lambda$ , then

$$(i.) E = 0 \text{ for } \lambda = \lambda_0 = \frac{12.348}{V} \text{ Å.U.}$$

(ii.) The maximum energy  $E_m$  occurs at  $\lambda_m = 1.3 \lambda_0$ , if  $\lambda_0 < 0.3 \text{ Å.U.}$

(iii.)  $E_m = kV^2$ , where  $k$  is a constant, provided the current is constant.

(iv.) The area of the curve,  $A$ , is given by  $A = k'V^2$ , where  $k'$  is a constant, provided the current is constant.

(v.)  $E$ , the energy at any wave-length, and  $A$ , the area of the curve, are both proportional to  $i$ , where  $i$  is the current through the tube.

#### *Empirical Law of Distribution.*

It is a simplification in the treatment to write  $x = \frac{\lambda - \lambda_0}{\lambda_0}$

and to consider the graphs wherein energy is plotted against  $x$ . The curves given by Dauvillier for voltages 71 kilovolt and 53.5 kilovolt and equal currents,  $0.5 \times 10^{-3}$  amp., have been redrawn to this new scale and are represented by the curves A and B, fig. 2. In this figure the scale of ordinates is arbitrary. If we denote energy by  $y$ .

then if  $y = f(x)$  is the empirical relation between  $y$  and  $x$ , we must have the following conditions :—

(i.)  $y = 0$  for  $x = 0$ .

(ii.)  $dy/dx = 0$  for  $x = h$ , where  $h = 0.3$ , giving a maximum value of  $y$ .

(iii.)  $y_{\max} = f(h) = kV^2$ .

(iv.)  $\int_0^\infty y \cdot dx = k_1 V^3$ .

(v.) The dependence of  $y$  on the current can be expressed by a further relation of the form  $y = i \cdot f(x)$ , where  $i$  is the current through the tube. If we can thus find the form of  $f(x)$  for any given current, the values of  $y$  for any other current can be found by multiplying by an appropriate factor. In the following, the experimental curves for a current 0.5 milliamp. have been employed as the basis of empirical calculations.

The analogy of the distribution curve for X-radiation to that for black body radiation suggested in the first place functions of the type governing the latter radiation. However, all such functions are ineffective on account of their failure to satisfy condition (i.) or difficulty in satisfying condition (iv.). It was thus decided to investigate some similar types of functions which would easily satisfy the conditions. A complete investigation was made of the function

$$y = (ax + bx^2 + cx^3) \cdot e^{-px},$$

which can be made to satisfy all the conditions. It was unfortunate that the constants of the curve, as determined by the conditions, gave two maxima and a minimum, whereas for slightly different values the curve only had one maximum.

Finally, the following function was examined and found to fit the experimental curves quite well.

We take

$$y = a(e^{-bx} - e^{-cx}).$$

This vanishes for  $x = 0$ .

Further,

$$dy/dx = a(-be^{-bx} + ce^{-cx})$$

and this has to vanish for  $x = h$ , giving

$$be^{-bh} - ce^{-ch} = 0.$$

For this value of  $x$  the maximum value of  $y$  is

$$y_m = a(e^{-bh} - e^{-ch}) = kV^2 = E_m, \text{ say,}$$

where  $E_m$  is the maximum arbitrary ordinate of any of the

56 Mr. M. H. Belz on the Distribution of curves. Finally,

$$\begin{aligned}\int_0^{\infty} y dx &= \int_0^{\infty} a(e^{-bx} - e^{-cx}) dx \\ &= a(1/b - 1/c) \\ &= k_1 V^3 = A, \text{ say,}\end{aligned}$$

where A is the arbitrary area of any of the curves.

We thus have the following equations :—

$$be^{-bh} - ce^{-ch} = 0, \quad . \quad . \quad . \quad . \quad (1)$$

$$ae^{-bh} - ae^{-ch} = E_m, \quad . \quad . \quad . \quad . \quad (2)$$

$$a/b - a/c = A. \quad . \quad . \quad . \quad . \quad (3)$$

From these we obtain

$$\frac{e^{bh}}{b} = \frac{e^{ch}}{c} = \frac{A}{E_m}, \quad . \quad . \quad . \quad . \quad (4)$$

and  $a$  follows from (2).

Let us now apply this to curve A, fig. 2, for which  $h = 0.3$ ,  $E_m = 12.54$ ,  $A = 28.71^*$ ,  $V = 71$  kv., and  $i = 0.5$  milliamp. We have  $A/E_m = 2.29$ .

To find the values of  $b$  and  $c$  as given by (4), it is most convenient to plot the curve  $y = \frac{e^{0.3x}}{x}$ , and obtain the values graphically. In this case we find  $b = 0.51$ , and  $c = 10.65$  approximately, the choice of  $b$  and  $c$  being such as to keep  $y$  positive for  $x > 0$ , which choice also gives  $d^2y/dx^2 < 0$  for  $x = h$ .

With these values of  $b$  and  $c$  we find, from (2),

$$a = 15.35.$$

Hence, we have

$$y = 15.35(e^{-0.51x} - e^{-10.65x}) \quad . \quad . \quad . \quad (5)$$

as the required relation.

In Table I. the results obtained from the empirical formula (5) and the experimental results are compared.

The curve obtained by means of the relation (5) is shown in fig. 2 by the curve A'.

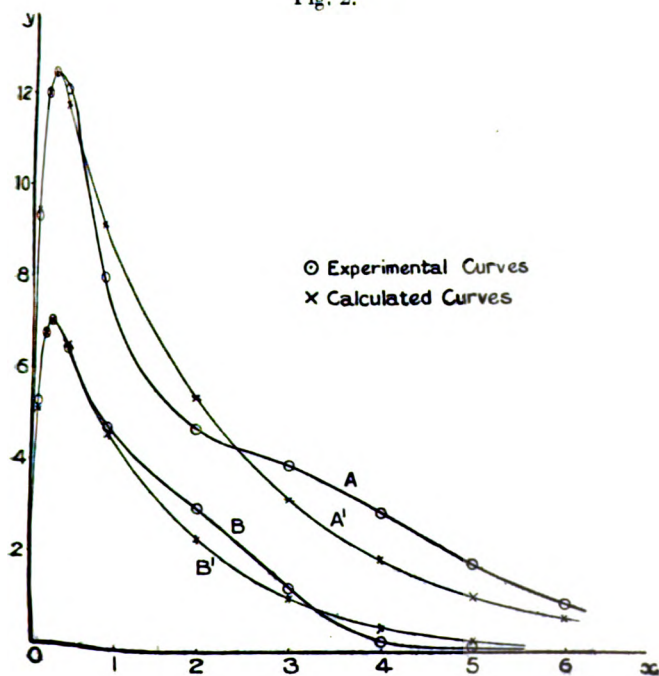
The fit of the two curves, A and A', is extremely good up to  $x = 0.7$ , and the subsequent departures are probably not greater than the experimental errors. It is difficult to

\* The areas given are those of the modified experimental curves which have been continued to become asymptotic to the X-axis.

TABLE I.

$x$ .	$y$ . calculated from (5).	$y$ . observed.
0.1	9.3	9.2
0.2	12.0	12.0
0.3	12.54	12.54
0.5	11.8	12.15
1.0	9.22	8.1
2.0	5.55	4.8
3.0	3.34	4.0
4.0	2.0	3.0
5.0	1.2	1.9
6.0	0.72	1.0

Fig. 2.





understand theoretically why the experimental curve A should have a point of inflexion in the neighbourhood of  $x = 3$ . The interchange of energy between the moving electron and the radiation will depend on the speed of the electron normal to the atoms of the target, and there seems no justification for assuming that there will be a proportionately large number of electrons giving rise to radiation in the neighbourhood of the point in question.

If we now consider curve B, fig. 2, for which  $h = 0.3$ ,  $E_m = 7.1$ ,  $A = 12.6$ ,  $V = 53.5$  kv., and  $i = 0.5$  milliamp., we find  $A/E_m = 1.776$ , and by means of the relation (4) we find  $b = 0.695$ ,  $c = 9.38$ , whence, by (2), we obtain  $a = 9.45$ .

We thus find

$$y = 9.45(e^{-0.695x} - e^{-9.38x}) \quad . \quad . \quad . \quad (6)$$

as the required relation.

In Table II. the results calculated from (6) are compared with the experimental results.

TABLE II.

$x$ .	$y$ calculated from (6).	$y$ observed.
0.1	5.12	5.3
0.2	6.77	6.8
0.3	7.10	7.10
0.5	6.605	6.5
1.0	4.71	4.85
2.0	2.46	3.1
3.0	1.17	1.35
4.0	0.585	0.25

Curve B', fig. 2, shows the results obtained from the relation (6). Here again the agreement between the observed and calculated curves is quite good.

We can thus state that the curves given by the general relation

$$y = a(e^{-bx} - e^{-cx}),$$

where the constants are determined in the above manner, represent to a very close approximation the curves observed experimentally.

*Application to Varying Potentials.*

It will now be shown how this empirical relation can be employed in the calculation of the energy distribution curve for a varying potential of definite period, such as is supplied by most types of high tension machines. For a practical illustration the case of a sinusoidal potential which has been rectified, so that both halves of the wave are operative, will be considered. The case of a more complicated wave form can be treated in a similar manner.

Consider, then, a sinusoidal potential for which

$$V_{\max} = 72.1 \text{ kv. and } i = 0.95 \text{ milliamp.,}$$

the current being constant. If we regard the half period as a unit of time, then provided this is sufficiently small compared with the time taken for measuring the intensity of the radiation emitted, we can regard the actual voltage as being equivalent to a number of components acting for definite fractions of the time unit, during each of which the voltage may be regarded as constant.

Fig. 3.

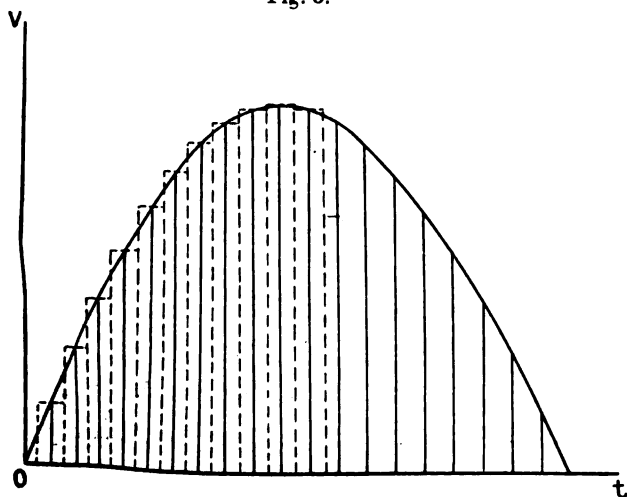


Fig. 3 shows the subdivision of the half period into twenty intervals. The corresponding ordinates at the ends of the intervals, in terms of the maximum ordinate, 72.1, are: 11.27, 22.3, 32.7, 42.4, 51, 58.4, 64.3, 68.6, 71.3, 72.1, etc. respectively. If we now further subdivide the curve as

shown by the dotted lines, we can state that the effect of the actual voltage will be equal to the sum of the following effects:—

(i.) One-twentieth of the effect of the constant potential 72.1 kv. and 0.95 milliamp.

(ii.) One-tenth of the effects of each of the following constant potentials and currents:—71.3 kv., 0.95 ma.; 68.6 kv., 0.95 ma., etc.

It is not necessary to consider seriously the effects of the voltages 11.27 and 22.3 kv., as these do not affect the position or intensity of the maximum. The calculation of each of the above effects can be very rapidly made. As illustration, the case of the first component will be worked out, and the results for the remaining components quoted. The same scale of ordinates will be preserved as in fig. 2, so that to obtain the distribution curve for any component for 0.95 ma. it is first necessary to find the curve for 0.5 ma. and then to multiply the ordinates by 1.9.

From the curves of fig. 2 we have

$$E_{0.5} = kV^2,$$

$$A_{0.5} = k_1 V^3,$$

where  $E_{0.5}$ ,  $A_{0.5}$ , mean the maximum energy and area corresponding to a current 0.5 ma.

From curve A, fig. 2, we find

$$k = \frac{E_{0.5}}{V^2} = \frac{12.54}{(71)^2} = 0.00249,$$

$$k_1 = \frac{A_{0.5}}{V^3} = \frac{28.71}{(71)^3} = 0.0000805,$$

while from curve B we find

$$k = 0.00248, \quad k_1 = 0.0000823.$$

We can thus take

$$k = 0.00249, \quad k_1 = 0.0000815.$$

Now for 72.1 kv., 0.5 ma. acting continuously, the maximum energy  $E_{0.5}$  is given by

$$\begin{aligned} E_{0.5} &= (72.1)^2 \times 0.00249 \\ &= 12.95, \end{aligned}$$

and for a current 0.95 ma. we obtain for the maximum energy

$$E_m = 24.6.$$

Also

$$A_{0.5} = (72.1)^3 \times 0.0000815 \\ = 30.5.$$

Hence

$$A/E_m = \frac{A_{0.5}}{E_{0.5}} = 2.35.$$

Since

$$\frac{e^{0.36}}{b} = \frac{e^{0.3c}}{c} = 2.35,$$

we find  $b = 0.5$ ,  $c = 10.8$ , and hence  $a = 29.9$ .

The formula for  $y$  now becomes

$$y = 29.9(e^{-0.5x} - e^{-10.8x}),$$

and Table III. gives the value of  $y$  corresponding to values of  $x$ .

TABLE III.

$x$ .....	0.5	1.0	2.0	3.0	4.0	5.0	6.0
$y$ .....	23.1	18.1	11.0	6.67	4.05	2.44	1.49

Now,

$$\lambda_0 = \frac{12.348}{72.1} = 0.171 \text{ \AA.U.},$$

and hence

$$\lambda_m = 1.3 \lambda_0 = 0.222 \text{ \AA.U.}$$

Also  $\lambda = \lambda_0(1+x)$ , and hence for the above values of  $x$  we find the following respective values of  $\lambda$ :—0.256, 0.343, 0.513, 0.684, 0.855, 1.026, 1.197 \text{ \AA.U.}

Since the supposed effect of this potential is only one-twentieth of the effect as calculated, it follows that on an energy wave-length graph we must plot the values given in the following Table IV.

TABLE IV.

$\lambda$ .....	0.171	0.222	0.256	0.343	0.513	0.684	0.855	1.026
$E$ .....	0	1.23	1.15	0.91	0.55	0.33	0.20	0.12

In exactly the same way we can calculate the effects of the other component potentials acting for their respective

times. The results of these calculations are summarized in Table V.

TABLE V.

Voltage in kilo- volts.	Energy wave-length coordinates.								
	$\lambda$								
71.3...	$\lambda$	0.173	0.2255	0.26	0.346	0.519	0.692	0.865	1.038
	E	0	2.4	2.27	1.78	1.1	0.66	0.4	0.24
68.6...	$\lambda$	0.18	0.234	0.27	0.36	0.54	0.72	0.90	1.08
	E	0	2.24	2.12	1.64	0.975	0.58	0.345	0.205
64.3...	$\lambda$	0.192	0.25	0.288	0.384	0.576	0.768	0.96	1.152
	E	0	1.96	1.805	1.375	0.792	0.453	0.26	0.15
58.4...	$\lambda$	0.212	0.276	0.318	0.424	0.636	0.828	1.06	1.272
	E	0	1.61	1.51	1.12	0.6	0.32	0.17	0.09
51.0...	$\lambda$	0.242	0.315	0.362	0.484	0.726	0.968	1.21	1.452
	E	0	1.32	1.212	0.822	0.362	0.16	0.07	0.03
42.4...	$\lambda$	0.292	0.38	0.438	0.584	0.876	1.168	1.46	1.752
	E	0	0.85	0.69	0.45	0.17	0.07	0.03	0.01

For the potential 32.7 kv. it is sufficient to plot the points  $\lambda = 0.378$ ,  $E = 0$ , and  $\lambda = 0.51$ ,  $E = 0.51$ , while for the potential 22.3 kv. it is sufficient to plot the points  $\lambda = 0.55$ ,  $E = 0$ ,  $\lambda = 0.8$ ,  $E = 0.236$ .

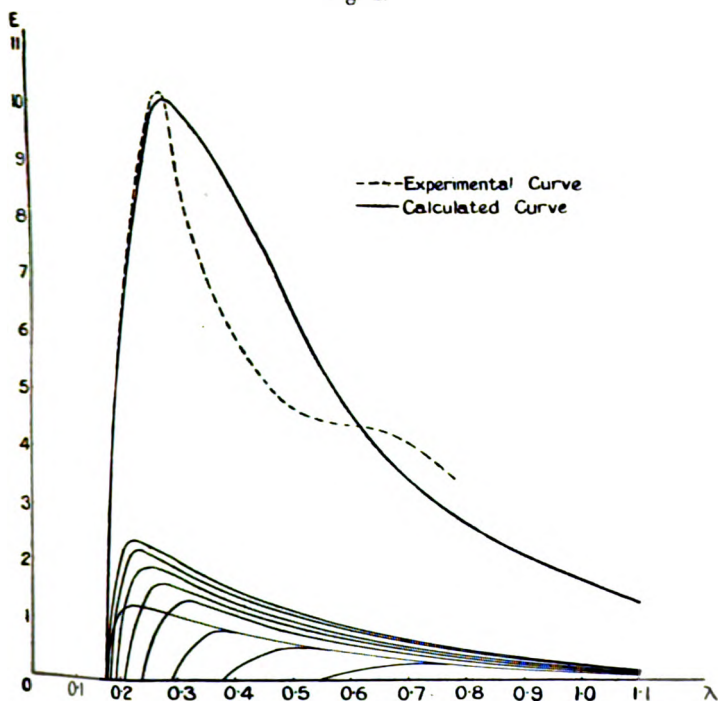
The results given in Tables IV. and V. and the preceding results have been plotted in fig. 4, on which is also drawn the sum of the ordinates of the component curves. This integral curve has the following characteristics:—

$$\lambda_0 = 0.171 \text{ Å.U.}, \lambda_m = 0.27 \text{ Å.U.}, E_m 10.1 \text{ units.}$$

The direct observation of the energy distribution curve for a sinusoidal voltage of frequency 50 per second, for which  $V_{\max.} = 72.1 \text{ kv.}$ ,  $i = 0.95 \text{ ma.}$ , has been made by Dauvillier (p. 75) for a Coolidge tube furnished with a radiator. He finds  $\lambda_0 = 0.171$  and  $\lambda_m = 0.26 \text{ Å.U.}$  For the same tube Dauvillier gives a curve for a constant potential 65.6 kv. and current 0.6 ma., and the ratio of the maximum energies of the two curves is approximately 0.795.

Now according to the above arbitrary choice of units for the measurement of energy, a standard Coolidge tube under a constant potential 65.6 kv. and current 0.6 ma. should have a maximum energy 12.9. Hence, the ratio  $E_m$  for the sinusoidal potential to  $E_m$  for the constant potential is  $10.1/12.9 = 0.784$ , and the agreement with the observed

Fig. 4.



ratio is well within the limit of experimental error. We can thus state that the empiric method gives the maximum energy in magnitude and position to an extremely good approximation. In the above calculations the potential wave has been divided into twenty intervals. The results obtained by a division into ten intervals only are in very good agreement with the above results, and hence for most practical purposes a subdivision into ten intervals is sufficient. The curve obtained by Dauvillier (curve B, p. 75) is shown in fig. 4 by the broken line. Comparing with the integral curve obtained above we find that the curves diverge

to the right of the maximum, the empiric curve lying above the observed curve. Hence, the empiric curve has a larger area than the observed curve. This difference may possibly be due to the use of a tube with a radiator, for if the constant potential curve for 65.6 kv., 0.6 ma. is drawn in the form of the  $x, y$  graph to the arbitrary scale used throughout, it is found that while the maximum energy satisfies the relation  $E_m = kV^2$ , the area of the curve falls short of the relation  $A = k_1 V^3$  by about 25 per cent. It thus seems likely that a standard tube under the sinusoidal potential and the current that has been examined should give greater energies to the right of the maximum than the radiator tube, and hence the agreement with the calculated curve will indeed be much better.

### *Extensions of the Method.*

The problem of determining the energy distribution curve when the form of the potential wave is less regular is solved in the same way as the above case. It is, of course, necessary to know the mean current through the tube and the maximum potential, and to have an oscillograph record of the potential wave. The experimental difficulties connected with this latter determination are very small, and the time taken to obtain a record will not disturb the routine of a large X-ray therapy department. The method used by Crowther\*, for example, is a very convenient one.

The whole of this discussion applies only to the continuous spectrum from a standard Coolidge tube. At the present stage it is not possible to consider the effect of the characteristic radiations for the reason that no experimental curves have been determined for constant potentials and corrected, as Dauvillier has done, to represent the true radiation from the target alone. Further, the radiations from a tube with a radiator, or a water-cooled tube, appear to obey laws slightly different from the radiations from a standard tube, and as these laws have not been investigated, we can at present only approximate to the radiations that they emit. For a gas tube the problem seems much more difficult, but

\* Crowther. *loc. cit.*, and also Camb. Phil. Soc. Proc. xxii. p. 68 (1924). Crowther shows that for a maximum potential of 73 kv. for a rectified transformer discharge, the current reaches saturation for a very small potential but increases slightly, probably due to the dragging out of additional electrons from the filament by the strong electrostatic field. This effect will probably be increased for higher voltages, and it thus seems advisable to obtain simultaneous records of the potential and current waves, as Crowther has done.

with systematic results it should not be insurmountable. What is most urgently required is a complete study of the radiations from all types of tubes under constant potentials from 30 kv. to 200 kv., say. The laws governing the continuous and the characteristic radiations could then be studied, and the determination of the energy distribution could be made a matter of precision. In addition it would be possible to state precisely, from a study of the oscillograph records, what potential and what current must be used to produce a maximum energy at a given wave-length.

The chief difficulty in any such systematic study lies in the generation of a constant potential. For moderate potentials a battery has been employed \*, but for the high potentials required in therapy treatment a battery is out of the question. The only method of such production is thus reduced to a form of high tension generating machine. Several devices have been suggested for generating an approximately constant potential. Ulrey† employed a step-up transformer using two kenotrons to rectify the current, and reduced the fluctuations by a specially-designed condenser, as suggested by Hull‡. No oscillograph records are shown, and the probability is that for very high tensions the fluctuations would be large. Dauvillier§ obtained a high potential by the rapid charge of a condenser, but does not consider that it would be possible to obtain 150 to 200 kv. in this way. Kirkpatrick|| used a synchronous shutter between the tube and the spectrometer to admit only the radiations corresponding to the peak voltage. This form of potential can hardly be called constant. More recently, Moore¶ has described a machine which is capable of producing high potentials which are very nearly constant, the oscillograph record showing small fluctuations about a constant mean. It is probably from machines of this type that we may expect to obtain the ideal form of potential. There is a growing tendency in X-ray practice to employ constant potential machines, and if this tendency becomes the rule a very large gap in the standardization of treatment will have been bridged.

\* Duane and Hunt, *Phys. Rev.* vi. p. 166 (1915).

† Ulrey, *Phys. Rev.* xi. p. 401 (1918).

‡ Hull, *Phys. Rev.* vii. p. 156 (1916).

§ Dauvillier, *Comptes Rendus*, clxii. p. 405 (1916).

|| Kirkpatrick, *loc. cit.*

¶ Moore, *Journ. Ront. Soc. (Brit. Journ. Radiology)* xx. p. 73 (1924).



Finally, it is of interest to note that Moppett \* has found evidence of a differential action of rays of varying wave-length on animal tissue. Using a Bragg spectrometer, adapted so that approximately equal energy was employed for each wave-length, he found that complete atrophy was produced in the chorio-allantoic membrane of eight-day chick embryos at the definite wave-lengths 0.11, 0.53, and 0.79 A.U. The effect was sharply restricted to these wave-lengths, the greatest effect occurring for the shortest wave-length. He concludes that the clinical uses of X-rays all correspond to stimulation by different wave-lengths. These results seem to indicate the necessity for a revision of the customary methods of dosage, as suggested earlier in the paper.

### *Summary.*

1. From the corrected experimental curves given by Dauvillier for a standard Coolidge tube under different constant potentials and currents, an empirical expression of the form

$$y = a(e^{-bx} - e^{-cx})$$

has been found to represent the energy distribution curve with considerable accuracy.

2. By subdividing the form of a sinusoidal potential wave into a number of intervals during which an appropriate constant potential is supposed to act, the application of the empirical expression produces an integral distribution curve, which agrees very well with an experimental curve given by Dauvillier for approximately equal conditions.

3. It is suggested that the energy distribution curve can, in the same way, be predicted when the forms of the potential and current waves are known.

4. The importance of the knowledge of the energy distribution curve for any type of machine in its application to clinical practice is stressed, and the method of standardizing treatment in terms of the characteristics of the energy distribution curve is suggested as being more precise than the former method of subjecting the patient to a certain number of erythema doses.

The remarks in this paper must necessarily be taken as preliminary on account of the relatively small amount of knowledge of the standard cases. As has been pointed out,

\* Moppett, *The Medical Journal of Australia*, i. no. 15, p. 364 (1925).

*Method of Determining Size of a Gravitating Particle.* 67

a complete discussion can only follow from thoroughly corroborated investigations of the energy distribution curves for different types of tubes under constant potentials up to 200 kilovolts. It is hoped shortly to obtain equipment in this University that will permit such an investigation.

It is a pleasure to thank Prof. T. H. Laby, Sc.D., who suggested the investigation, and Prof. J. H. Michell, F.R.S., for helpful suggestions during the course of this research.

[I am indebted to Dr. Dauvillier for drawing my attention, after he had read the above in manuscript, to a paper by Behnken on the same subject—a paper which was not accessible to Mr. Belz. References to Behnken's papers have been added.—T. H. L.]

The University,  
Melbourne.  
July 13, 1925.

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V. *A supposed Relativity Method of Determining the Size of a Gravitating Particle.* By Prof. H. T. H. PIAGGIO, M.A., D.Sc., and J. CRITCHLOW, B.Sc., University College, Nottingham\*.

*Introduction.*

A PARTICULAR solution of Einstein's gravitational equations for an isolated particle is the well-known form, first obtained by Schwarzschild,

$$ds^2 = -\gamma^{-1} dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta d\phi^2 + \gamma dt^2, \quad (1)$$

where  $\gamma = 1 - 2m/r$ .

$m$  is a constant subsequently identified with the mass of the particle.

Now when  $r$  has the value  $2m$ , the coefficient of  $dr^2$  in (1) is infinite. This result has generally been interpreted as showing that an impassable barrier exists of radius  $2m$ , and thus that a particle must have a definite size determined by its mass.

The object of this paper is to give reasons for rejecting this interpretation, and for considering the singularity as a purely mathematical property of a certain transformation of coordinates, without any physical significance. It will be shown that alternative solutions exist, which satisfy all the physical tests applicable and yet do not exhibit this singularity. One of these solutions was actually given by

\* Communicated by the Authors.

Schwarzschild himself. It will be pointed out that although one solution can always be transformed into another, this transformation is not valid for all values of the variable.

In the usual method of obtaining (1) this limitation is overlooked. The apparent singularity arises when we attempt to give the variable a value for which the transformation is illegitimate.

*Alternative Solutions of the Gravitational Equations  
for an Isolated Particle.*

The simplest method of obtaining alternative solutions is to transform (1) by the relation

$$r=f(R).$$

We must now consider what forms for the function  $f$  are physically possible. It will be remembered that in the deduction of (1),  $r$ ,  $\theta$ ,  $\phi$ ,  $t$  are at the outset merely four variables whose exact significance is unknown. When we endeavour to identify them with the ordinary polar coordinates and the time, we take our solution and see if it satisfies the following requirements:—

- (i.) it must possess spherical symmetry in space ;
- (ii.) it must possess symmetry as regards past and future time ;
- (iii.) for very large values of  $r$  it must tend to the form  $ds^2 = -dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta d\phi^2 + dt^2$  ;
- (iv.) it must, when applied to the sun, agree with the Newtonian theory and ordinary astronomical observations to the first order ;
- (v.) it must give, as second order effects, the advance of the perihelion of Mercury, the deflexion of light passing near the sun, and the spectral shift observed for the sun and for the companion of Sirius.

Now these requirements are satisfied by Schwarzschild's solution, but they are also satisfied by other solutions. A well-known example is Hill and Jeffery's isotropic solution

$$ds^2 = -(1+m/2R)^4 (dR^2 + R^2 d\theta^2 + R^2 \sin^2 \theta d\phi^2) + \left\{ \frac{1-m/2R}{1+m/2R} \right\}^2 dt^2, \quad \dots (2)$$

which can be obtained from (1) by the transformation

$$r=(1+m/2R)^2 R.$$

This is more complex mathematically than (1), but it satisfies all the requirements stated above. As Eddington \* says, "this system of coordinates is naturally arrived at when we partition space by rigid scales or by light-triangulations in a small region, *e. g.* in terrestrial measurements." From a physical point of view the  $R$  of (2) has therefore at least as good a claim to be identified with the actual radius vector from the sun as the  $r$  of (1). Of course in either case the identification cannot be exact, for when we speak of the actual radius vector we are tacitly assuming a Euclidean universe, whereas Einstein's equations imply that it is non-Euclidean.

The isotropic solution is the best known of the alternative solutions, but others are easily obtained by the transformation  $r = f(R)$ , where the only limitation on the form of the function is that the limit of the ratio  $r/R$  should be unity as  $r$  approaches infinity.

By putting  $r = (R^3 + 4m^2)^{1/2}$ , (1) becomes

$$ds^2 = -\{1 + 2m(R^3 + 4m^2)^{-1/2}\} dR^2 - (R^3 + 4m^2)(d\theta^2 + \sin^2 \theta d\phi^2) + \{1 - 2m(R^3 + 4m^2)^{-1/2}\} dt^2. \quad (3)$$

Similarly by putting  $r = (R^3 + 8m^3)^{1/3}$ , (1) becomes

$$ds^2 = -\frac{(R^3 + 8m^3)^{-4/3} R^4 dR^2}{1 - 2m(R^3 + 8m^3)^{-1/3}} - (R^3 + 8m^3)^{2/3}(d\theta^2 + \sin^2 \theta d\phi^2) + \{1 - 2m(R^3 + 8m^3)^{-1/3}\} dt^2. \quad (4)$$

More generally, we could put

$$r = (R^n + 2^n m^n)^{1/n}.$$

It is sometimes overlooked that (1) is not the solution that Schwarzschild originally obtained. On referring to his paper †, we find that he started with a somewhat complicated solution in  $x_1, x_2, x_3, x_4$ . By putting

$$x_1 = r^3/3, \quad x_2 = -\cos \theta, \quad x_3 = \phi, \quad x_4 = t,$$

he obtained a second form

$$ds^2 = -\frac{(r^3 + \rho)^{-4/3} r^4 dr^2}{1 - \alpha(r^3 + \rho)^{-1/3}} - (r^3 + \rho)^{2/3}(d\theta^2 + \sin^2 \theta d\phi^2) + \{1 - \alpha(r^3 + \rho)^{-1/3}\} dt^2 \quad (5)$$

containing the two constants  $\alpha$  and  $\rho$ .

\* 'Mathematical Theory of Relativity,' p. 93.

† Berlin. *Sitzungsberichte*, 1916, p. 189; most of it is reproduced in Rice's 'Relativity,' pp. 271-276.

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Finally, by writing  $R=(r^3+\rho)^{1/3}$ , he obtained a form equivalent to (1).

It will be noticed that if we put  $\rho=\alpha^3=(2m)^3$ , (5) reduces to (4).

### *Comparison of these Solutions.*

As we noted at the outset, the coefficient of  $dr^2$  in (1) becomes infinite when  $r=2m$ . In (2) the coefficient of  $dR^2$  becomes infinite for  $R=0$ , but not for any positive value of  $R$ . In (3) and (4) the coefficient of  $dR^2$  is always finite for positive values of  $R$ . (5) cannot be discussed until we know the sign of  $\rho-\alpha^3$ .

Thus the singularity that appears in (1) does not appear in the other forms that are equally in accord with the only physical evidence available, and it is repugnant to the spirit of relativity to attach a physical interpretation to a property of a special form of coordinates.

Similar considerations apply to the coefficient of  $dt^2$ . In (1) this coefficient becomes zero when  $r=2m$ , and tempts us to speak of a standstill of time at this region; but again we reject this interpretation upon noticing that the coefficient of  $dt^2$ , which may vanish in (1) or (2), cannot do so in (3) or (4) for any positive value of  $R$ .

### *Limitations to the Validity of Transformations.*

We shall now consider how it is that Schwarzschild's third form (1) exhibits a singularity which, when  $\rho-\alpha^3$  is positive or zero, is not possessed by his second form (5).

The transformation he used, namely

$$R=(r^3+\rho)^{1/3},$$

imposes a distinct limitation upon  $R$ . Since  $r$  is, for a physical interpretation, restricted to real positive values from 0 to  $\infty$ ,  $R$  has a minimum value  $\rho^{1/3}$ . If we take  $\rho=\alpha^3$ , a very natural assumption, designed to give (5) a singularity at  $r=0$ , where it might be expected, we unconsciously introduce a singularity into (1) for the corresponding value  $\alpha (=2m)$  of  $R$ .

It is more usual now to obtain Schwarzschild's third form directly\*. Starting with the form

$$ds^2 = -U(r) dr^2 - V(r)(r^2 d\theta^2 + r^2 \sin^2\theta d\phi^2) + W(r) dt^2,$$

a simplification is introduced by the transformation

$$r_1^2 = r^2 V(r). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

\* Cf. Eddington, p. 83.

This transformation may only be valid for a restricted range of values of  $r$ . For example, if  $V(r)=1+4m^2/r^2$ ,

$$r_1^2=r^2+4m^2.$$

In this case  $r_1$  cannot be less than  $2m$ . It is therefore natural that a singularity should arise when  $r_1=2m$ , whereas in the more general form such a singularity might have been present only at the obvious point  $r=0$ .

### Summary.

A singularity in Schwarzschild's solution of Einstein's equations which has been widely interpreted as indicating a definite size for a gravitating particle, is shown to be merely a mathematical property of a transformation of coordinates, without any physical significance.

Nottingham,  
October 10th, 1925.

## VI. On the Concentration of Stress in the Neighbourhood of a Small Spherical Flaw; and on the Propagation of Fatigue Fractures in "Statistically Isotropic" Materials. By R. V. SOUTHWELL, M.A., F.R.S., and H. J. GOUGH, M.B.E., B.Sc., of the National Physical Laboratory\*.

1. **T**HE mathematical theory of elasticity, as at present developed, predicates two essential qualities in the ideal substances with which it is concerned: they must be *elastic*, so that the deformation produced by any system of applied forces will disappear when that system is removed; and they must be *continuous*, so as to be capable of indefinite subdivision without losing any property which they exhibit in bulk.

It is probable that those characteristics of real substances which are described by the terms "plasticity" and "hysteresis" will in time, by suitable extensions of the theory, be brought within its scope †; but the assumption of continuity appears to be fundamental, and results which have this basis should be applied with considerable reserve to actual cases

\* Communicated by the Authors.

† A beginning has been made by Volterra and others. Cf. A. E. H. Love, 'Mathematical Theory of Elasticity', §82 and footnote; L. Prandtl, *Zeitsch. für angewandte Math. u. Mech.*, vol. iii, pp. 401-406 (1923); H. Hencky, *ibid.*, vol. iv, pp. 323-334 (1924); and a paper in 'Engineering', Aug. 23, 1912.

of stress-concentration, because the structure of the material must be expected to play an important part\*. Thus we cannot look for much direct assistance from theory when attacking such problems as the mechanism of fracture in engineering materials or the factors which limit their ultimate strength. Fracture is a consequence of high stresses,—presumably (since it occurs under average stresses which are far below the calculated “cohesion”) of intense local concentration of stress; and we know that most engineering materials are aggregates of metallic crystals which individually are very far from being isotropic, and which are arranged at random, without any tendency towards a definite orientation. We cannot say in advance how the planes of greatest weakness will lie in a given region of concentrated stress: their direction may be such as will relieve the stress-concentration, but it is equally likely to have no such effect. We are in a field of problems where exact calculations can have no place, and occurrences are governed by probabilities.

In this field, on the other hand, the mathematical theory may still have some value as a statistical method. The crystalline aggregate is in general statistically homogeneous, and unless the individual crystals have been violently distorted by special treatment, such as “cold work”, it will also be statistically isotropic. Alternating or fluctuating stresses, which produce distortion of the material as a whole, are not likely to have seriously affected this statistical homogeneity and isotropy of the aggregate, even though they are sufficiently intense to have caused some plastic slipping†. Thus the theory, although it can give no trustworthy indication of the actual stresses which have brought about failure in any particular instance, may be used with some confidence to determine *the relative values of their probable intensities at different points in the material*; and in this way it may serve to elucidate the sequence of events in a given fracture, or even to suggest, as a matter of probabilities, its primary cause.

2. An attempt to apply the mathematical theory in this way was made by one of us in 1921, in a paper written for the Materials Sub-Committee of the Aeronautical Research

\* Cf. A. A. Griffith, Phil. Trans. Roy. Soc. A, vol. 221. p. 193 (1920).

† For the argument of this paper, it is only necessary to assume that the crystalline structure is sensibly uniform in kind over regions which are large in comparison with individual crystals. This assumption may not be justified in the neighbourhood of a skin formed by the process of “case-hardening”, or in regions where localized plastic strain has occurred under an intense concentration of stress.

Committee on the subject of "spiral fractures" in the propeller shafts of aero-engines. Prof. C. F. Jenkin, in his Presidential Address to Section G at the 1920 meeting of the British Association, had directed attention to a fracture of this nature (illustrated in fig. 1\*) as a phenomenon which had not so far received a satisfactory explanation, although possessing great interest and practical importance from the point of view of the designer. "It is, of course, a fatigue fracture—*i.e.*, it spread gradually. The questions to be answered are, Did it fail under tension, bending or torsion? and, Why was a spiral direction followed by the failure as it spread?" †

It seemed fairly clear (since there was no reason to believe that the helicoidal surface of the fracture had been a surface of special weakness in the shaft when new) that the crack had followed a path which was determined primarily by the distribution of stress in the material; and a consideration of probabilities, based on a theoretical solution for the stress-distribution round a small spherical flaw in isotropic elastic material, indicated that a fatigue fracture, *in material which is statistically isotropic*, has a strong tendency to spread along a surface which is tangential at every point to the plane of the greatest principal tensile stress. (On the basis of this result, it appeared that the answers to Prof. Jenkin's questions could be stated as follows:—The action which induced his "spiral fracture" was in the main torsional. Tension, bending, or compression may have contributed in a minor degree, and an idea of the relative importance of these actions in any particular instance could be obtained from an examination of the direction followed by the fracture. Failure began at some point where there was an intense local concentration of stress (probably caused by a flaw in the material, or by a surface scratch), and a "spiral" direction was followed by the failure (*i.e.*, the surface of separation is, in its general features, helicoidal) because the tensile stresses induced by torsion attain their maximum values on a surface of this type.

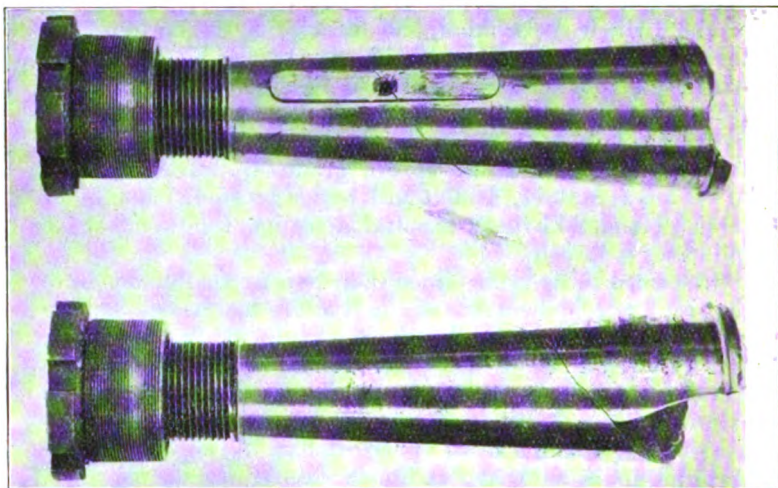
To prevent misunderstanding, it was emphasized that the existence of a localized crack in an elastic solid body must modify to some extent, and may alter very considerably, the stress-distribution which a given system of applied forces will entail; thus it is not certain that we shall be able to

\* We are indebted to Prof. Jenkin for the loan of the photographs reproduced in this figure. Other photographs of typical fractures are given in the plate facing p. 14 of his 'Report on Materials of Construction used in Aircraft and Aircraft Engines' (1920).

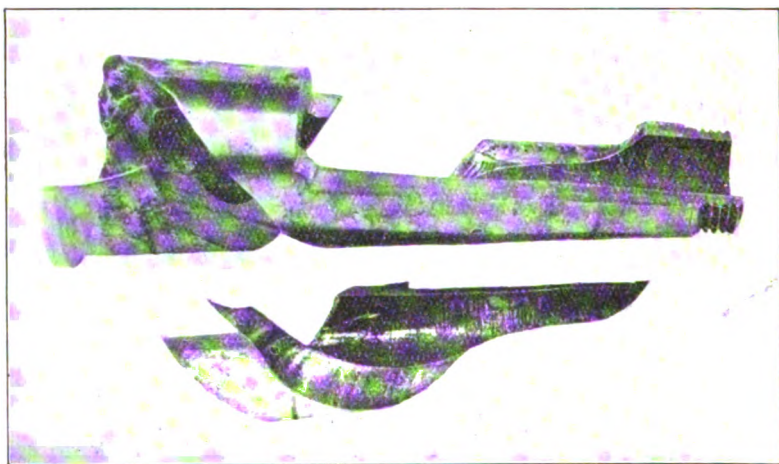
† British Association Report, 1920, p. 131.



Fig. 1.



Spiral Fracture in Crankshaft, commencing at the bottom corner of the Keyway.



The same shaft, cut open.

foretell the path of a fatigue fracture, provided only that we can calculate the theoretical stress-system which obtains before any crack has formed. But within its limitations it appeared that the theory should prove useful in the diagnosis of fatigue fractures; and conversely, that an examination of a large number of fatigue fractures might be expected to reveal more clearly what these limitations are.

3. These conclusions, and the arguments by which they were reached (stated more fully in §§ 4 to 8 below), were generally accepted. The paper mentioned has been the subject of considerable discussion by the Elasticity and Fatigue Panel of the Aeronautical Research Committee, aimed in the main at determining what, if any, is the bearing of its results upon the more difficult question of the origin of fatigue fractures; and arising out of this discussion certain experiments have been conducted in the Engineering Department of the National Physical Laboratory. The present paper has been written at the request of the Panel, to summarize the position now attained. We are conscious that our ideas have been largely influenced by those of other members, to whom (and especially to Dr. A. A. Griffith) we desire to express our indebtedness; but it should be emphasized that the Panel is not in any way responsible for the views herein expressed.

Our thanks are also due to Miss C. G. C. Phillips, who prepared the line diagrams which illustrate this paper.

## Part I.—THE PROPAGATION OF FATIGUE FRACTURES.

### *Stress-Concentration produced by a Small Spherical Flaw in Material subjected to Uniform Tension.*

4. We require first of all to determine the stress-system which obtains in the neighbourhood of a small spherical flaw when the stress at points far away from the flaw is a uniform tension  $T$  in one direction only. This is a problem of symmetrical strain in a solid of revolution\*, and the stress-equations of equilibrium, expressed in terms of cylindrical coordinates  $r, \theta, z$ , are

$$\left. \begin{aligned} \frac{\partial \hat{r}r}{\partial r} + \frac{\partial r\hat{z}}{\partial z} + \frac{\hat{r}r - \theta\hat{\theta}}{r} &= 0, \\ \frac{\partial r\hat{z}}{\partial r} + \frac{\partial \hat{z}z}{\partial z} + \frac{\hat{r}z}{r} &= 0. \end{aligned} \right\} \dots \dots (1)$$

\* Cf. Love, *op. cit.*, § 188.

It can be verified by substitution that these stress-equations will be satisfied if we assume \*

$$\left. \begin{aligned} \widehat{rr} &= \frac{\partial}{\partial z} \left\{ \sigma \nabla^2 \chi - \frac{\partial^2 \chi}{\partial r^2} \right\}, \\ \widehat{\theta\theta} &= \frac{\partial}{\partial z} \left\{ \sigma \nabla^2 \chi - \frac{1}{r} \frac{\partial \chi}{\partial r} \right\}, \\ \widehat{zz} &= \frac{\partial}{\partial z} \left\{ (2-\sigma) \nabla^2 \chi - \frac{\partial^2 \chi}{\partial z^2} \right\}, \\ \widehat{rz} &= \frac{\partial}{\partial r} \left\{ (1-\sigma) \nabla^2 \chi - \frac{\partial^2 \chi}{\partial z^2} \right\}, \end{aligned} \right\} \dots (2)$$

where  $\sigma$  is Poisson's ratio,  $\nabla^2$  denotes the operator

$$\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2},$$

and  $\chi$  is a function of  $r$  and  $z$  which satisfies the equation

$$\nabla^4 \chi = 0. \dots (3)$$

Further, it can be shown that the strains deduced from the expressions (2) are compatible. The boundary conditions require that at a great distance from the centre of the spherical flaw

$$\widehat{rr} = \widehat{\theta\theta} = \widehat{rz} = 0, \quad \widehat{zz} = T, \dots (4)$$

and that the surface of the flaw shall be free from stress.

5. A solution of (2) and (3) which satisfies these boundary conditions is most easily obtained by transformation into spherical coordinates, with origin at the centre of the flaw †. We find as the required expression for the stress-function  $\chi$

$$\chi = \frac{1}{14-10\sigma} \left[ \frac{(1-2\sigma)z^3 + 3\sigma r^2 z}{6(1+\sigma)} - \frac{a^3}{14-10\sigma} \left\{ (1-5\sigma) \sinh^{-1} \left( \frac{z}{r} \right) + 5 \frac{z}{R} - \frac{a^2 z}{R^3} \right\} \right],$$

where  $a$  is the radius of the flaw, and

$$R^2 = r^2 + z^2.$$

This expression can be shown to satisfy (3), and it gives

\* *Ibid.*, equations (63) to (65).

† The complete analysis is contained in a paper not yet published, "On some Stress-Systems in Solids of Revolution".

as corresponding expressions for the stress-components (2)

$$\left. \begin{aligned} \widehat{rr} &= \frac{T}{14-10\sigma} \cdot \frac{a^3}{R^3} \left[ 9-15\sigma-12 \frac{a^2}{R^2} \right. \\ &\quad \left. - \frac{r^2}{R^2} \left( 72-15\sigma-105 \frac{a^2}{R^2} \right) + 15 \frac{r^4}{R^4} \left( 5-7 \frac{a^2}{R^2} \right) \right], \\ \widehat{\theta\theta} &= \frac{T}{14-10\sigma} \cdot \frac{a^3}{R^3} \left[ 9-15\sigma-12 \frac{a^2}{R^2} \right. \\ &\quad \left. - 15 \frac{r^2}{R^2} \left( 1-2\sigma-\frac{a^2}{R^2} \right) \right], \\ \widehat{zz} &= T \left[ 1 - \frac{1}{14-10\sigma} \cdot \frac{a^3}{R^3} \left\{ 38-10\sigma-24 \frac{a^2}{R^2} \right. \right. \\ &\quad \left. \left. - \frac{r^2}{R^2} \left( 117-15\sigma-120 \frac{a^2}{R^2} \right) + 15 \frac{r^4}{R^4} \left( 5-7 \frac{a^2}{R^2} \right) \right\} \right], \\ \widehat{rz} &= \frac{T}{14-10\sigma} \cdot \frac{a^3 z r}{R^5} \left[ -3(19-5\sigma) + 60 \frac{a^2}{R^2} \right. \\ &\quad \left. + 15 \frac{r^2}{R^2} \left( 5-7 \frac{a^2}{R^2} \right) \right]. \end{aligned} \right\} \quad (5)$$

Fig. 2 shows the system of coordinates to which these equations relate. At points in the  $(r, \theta)$  plane OB, where  $z=0$ , the foregoing expressions (5) for the stress-components reduce to

$$\left. \begin{aligned} \widehat{rr} &= \frac{12T}{14-10\sigma} \cdot \frac{a^3}{R^3} \left( 1 - \frac{a^2}{R^2} \right), \\ \widehat{\theta\theta} &= \frac{3T}{14-10\sigma} \cdot \frac{a^3}{R^3} \left( -2 + 5\sigma + \frac{a^2}{R^2} \right), \\ \widehat{zz} &= T \left[ 1 + \frac{1}{14-10\sigma} \cdot \frac{a^3}{R^3} \left( 4-5\sigma + 9 \frac{a^2}{R^2} \right) \right], \\ \widehat{rz} &= 0, \end{aligned} \right\} \quad (6)$$

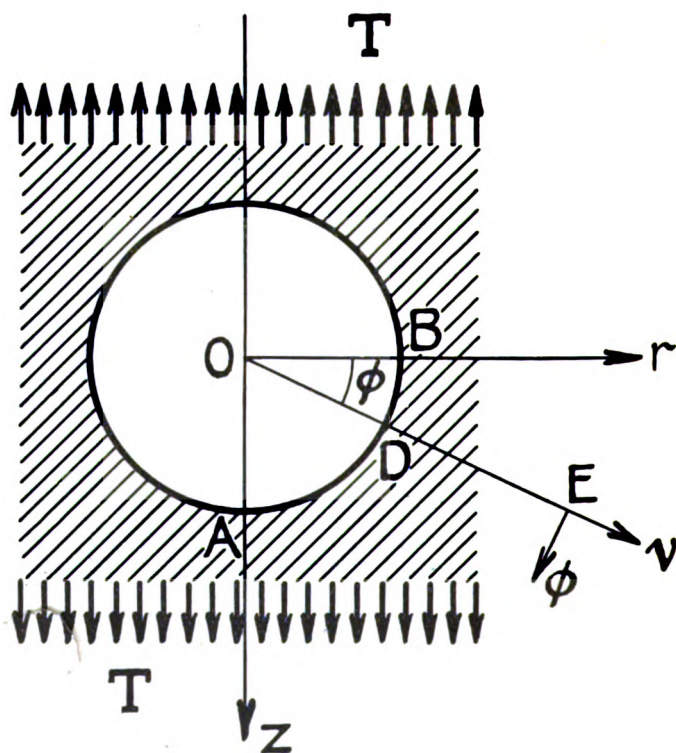
where  $R$  is now identical with  $r$ .

Making  $a/R$  equal to unity in these expressions, we see that at points such as B, where the  $(\theta, z)$  plane intersects the surface of the flaw,  $\widehat{zz}$  has the value  $3(9-5\sigma)T/(14-10\sigma)$ , which is slightly greater than  $2T$  when  $\sigma=0.3$  (a representative value for steel). If the flaw had been cylindrical, with its axis perpendicular to the direction of  $T$ , the corresponding extreme value of  $\widehat{zz}$  would have been  $3T^*$ , whence

\* Cf. A. Morley, 'Strength of Materials' (4th Edition), Appendix, p. 537.

it is clear that the spherical flaw produces a less serious intensification of stress: this result might, of course, have been expected from physical considerations. *In neither case is the intensification dependent on the actual magnitude of the flaw, provided only that this is infinitesimal in comparison with the external dimensions of the elastic solid considered.*

Fig. 2.

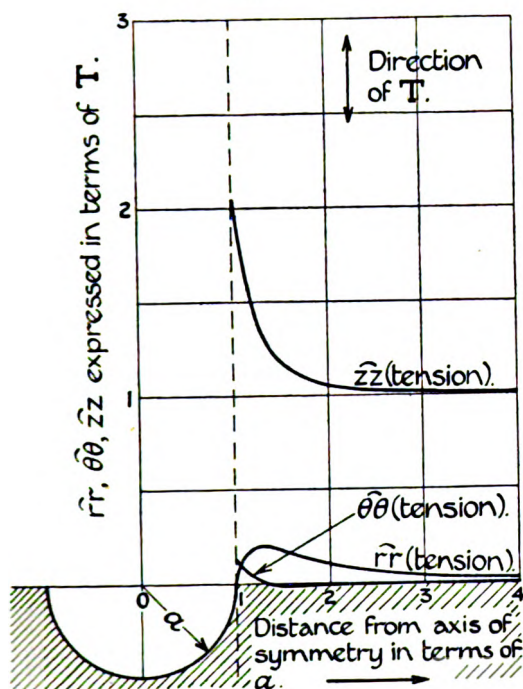


The values of  $\hat{z}z$  at other points in the  $(r, \theta)$  plane OB are plotted in fig. 3 ( $\sigma$  being given, as before, the value 0.3), together with those of  $\hat{r}r$  and  $\hat{\theta}\theta$  for the same plane. The nature of the variations in  $\hat{r}r$  and  $\hat{z}z$  is generally similar to what is found in the corresponding solution for a cylindrical flaw\*, as will be evident from the curves given, for purposes

\* Cf. A. Morley, *op. cit.*, p. 538.

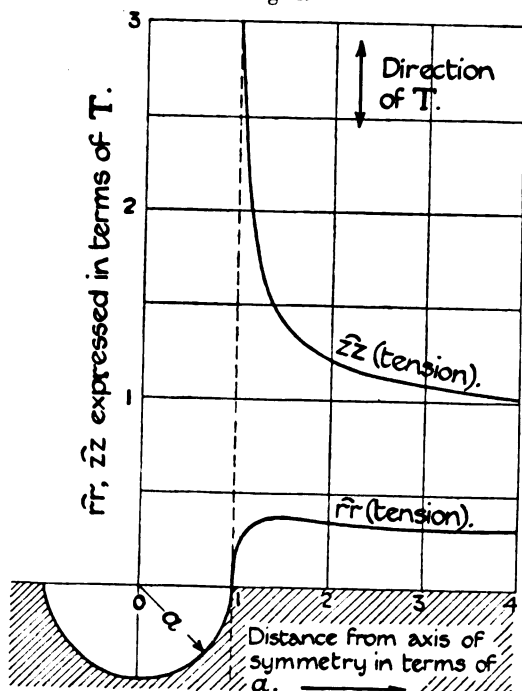
of comparison, in fig. 4. The analytical expressions for the stress-components are, however, much simpler in the latter solution, since they have the property, characteristic of any two-dimensional system in which the tractions on the boundaries are specified, of being independent of the value of  $\sigma$ .

Fig. 3.



From the nature of the curves given in fig. 3, it will be evident that, on any theory of breakdown, the dominant part is played by the increased tension  $\hat{z}\hat{z}$  at points close to the surface of the flaw. Moreover, we can show that this intensification of stress at the surface is confined to points which are near to the  $(r, \theta)$  plane,—i. e., to points of which the angular coordinate  $\phi$  (fig. 2) is small. For if we consider a cone of which the trace is ODE (fig. 2), we have, corresponding to the stresses  $\hat{r}\hat{r}$ ,  $\hat{\theta}\hat{\theta}$ , and  $\hat{z}\hat{z}$  for the  $(r, \theta)$  plane, the stresses  $\hat{\nu}\hat{\nu}$ ,  $\hat{\theta}\hat{\theta}$ , and  $\hat{\phi}\hat{\phi}$  respectively. If the directions

Fig. 4.



of  $\nu$  and  $\phi$  are as specified in fig. 2, we have the scheme of transformation

	$r$	$\theta$	$z$
$\nu$	$\cos \phi$	0	$\sin \phi$
$\theta$	0	1	0
$\phi$	$-\sin \phi$	0	$\cos \phi$

and from the usual formulæ for transformation of stress-components\* we obtain

$$\left. \begin{aligned} \hat{\nu\nu} &= \hat{r\hat{r}} \cos^2 \phi + \hat{z\hat{z}} \sin^2 \phi + \hat{z\hat{r}} \sin 2\phi, \\ \hat{\phi\phi} &= \hat{r\hat{r}} \sin^2 \phi + \hat{z\hat{z}} \cos^2 \phi - \hat{z\hat{r}} \sin 2\phi, \\ \hat{\nu\phi} &= \frac{1}{2}(\hat{z\hat{z}} - \hat{r\hat{r}}) \sin 2\phi + \hat{z\hat{r}} \cos 2\phi. \end{aligned} \right\} \quad (7)$$

\* A. E. H. Love, *op. cit.*, § 49.

Then from (5) and (7) (writing  $\cos \phi$  for  $r/R$  and  $\sin \phi$  for  $z/R$  in the former equations) we have, as expressions corresponding to (6'),

$$\left. \begin{aligned} \widehat{\nu} &= T \left[ \sin^2 \phi + \frac{1}{14-10\sigma} \cdot \frac{a^3}{R^3} \right\} -38 + 10\sigma \\ &\quad + 24 \frac{a^2}{R^2} + \left( 50 - 10\sigma - 36 \frac{a^2}{R^2} \right) \cos^2 \phi \left. \right\}, \\ \widehat{\theta\theta} &= \frac{T}{14-10\sigma} \cdot \frac{a^3}{R^3} \left[ 9 - 15\sigma - 12 \frac{a^2}{R^2} \right. \\ &\quad \left. - 15 \left( 1 - 2\sigma - \frac{a^2}{R^2} \right) \cos^2 \phi \right], \\ \widehat{\phi\phi} &= T \left[ \cos^2 \phi + \frac{1}{14-10\sigma} \cdot \frac{a^3}{R^3} \left\{ 9 - 15\sigma - 12 \frac{a^2}{R^2} \right. \right. \\ &\quad \left. \left. - \left( 5 - 10\sigma - 21 \frac{a^2}{R^2} \right) \cos^2 \phi \right\} \right], \\ \widehat{\nu\phi} &= \frac{T}{2} \sin 2\phi \left[ 1 \right. \\ &\quad \left. + \frac{1}{14-10\sigma} \cdot \frac{a^3}{R^3} \left\{ 10(1+\sigma) - 24 \frac{a^2}{R^2} \right\} \right]. \end{aligned} \right\} \quad (8)$$

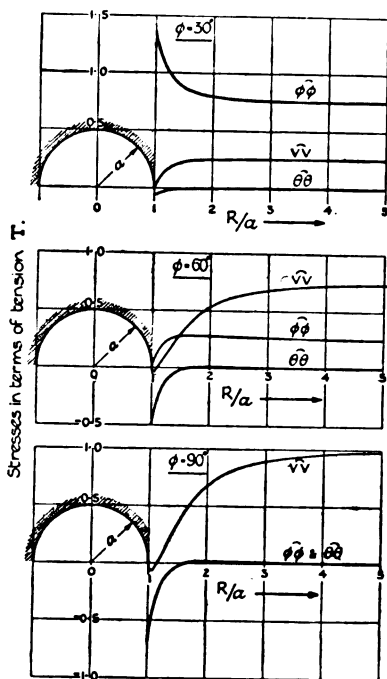
Curves similar to those of fig. 3 can now be plotted for any value of  $\phi$ , and fig. 5 shows the forms which they assume when  $\phi = 30^\circ$ ,  $60^\circ$ , and  $90^\circ$ . At the surface of the flaw the stress-components attain values given by

$$\left. \begin{aligned} [\widehat{\nu}]_{R=a} &= [\widehat{\nu\phi}]_{R=a} = 0, \\ [\widehat{\theta\theta}]_{R=a} &= \frac{3T}{14-10\sigma} [-(1+5\sigma) + 10\sigma \cos^2 \phi], \\ [\widehat{\phi\phi}]_{R=a} &= \frac{3T}{14-10\sigma} [-(1+5\sigma) + 10 \cos^2 \phi], \end{aligned} \right\} \quad (9)$$

and fig. 6, in which the values reached by  $\widehat{\theta\theta}$  and  $\widehat{\phi\phi}$  at the surface of the flaw are exhibited by means of a polar diagram, shows clearly the extent to which the intensification of the stresses is a localized effect. It is evident that the maximum stress, strain and stress-difference will occur at points such as B on the  $(r, \theta)$  plane in fig. 2, so that a fracture may be expected to start at one of these points.



Fig. 5.



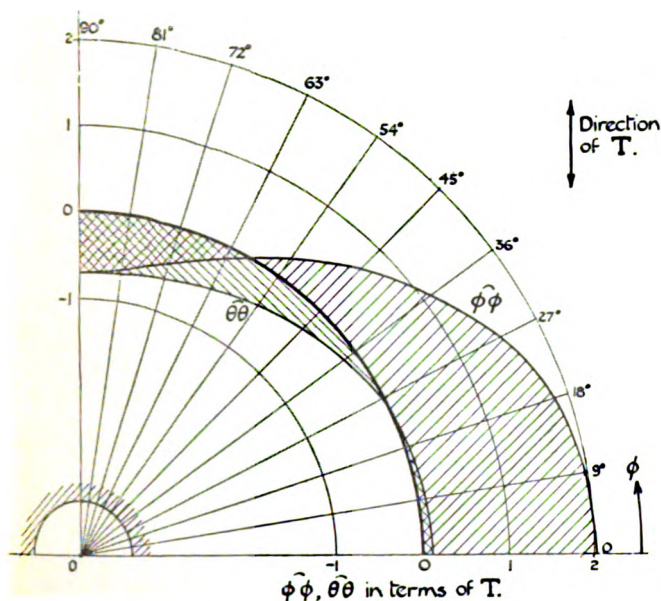
*Extension to Compound Stress-Systems. Effect of a Small Spherical Flaw in a Twisted Shaft.*

6. The stresses introduced by the flaw upon planes which contain the axis of symmetry are, as we have seen, purely normal. They will be represented by  $\hat{\theta}\theta$ , and from fig. 6 can be seen to be of the same sign as  $\hat{T}$  in the neighbourhood of B, and of opposite sign, and in magnitude approximately equal to  $2/3T$ , in the neighbourhood of A.

Suppose, now, that the original stress-system consists of two principal stresses, and let us consider the stress-system, in the neighbourhood of the flaw, which corresponds to each separately. The  $(r, \theta)$  plane for the first system will be a  $(z, r)$  plane for the second, and *vice versa*; hence, the combined effect on the plane OB (fig. 2) will consist of the  $\hat{z}z$  stresses for the first system, as given in fig. 3, combined with the  $\hat{\theta}\theta$  stresses corresponding to the second system, as given (for points lying on the surface of the flaw) in fig. 6. The second system will increase the stress at some points

of the circular boundary, and will decrease it at others; the resultant effect of two principal stresses which have given magnitudes will evidently be greatest when they have opposite signs.

Fig. 6.



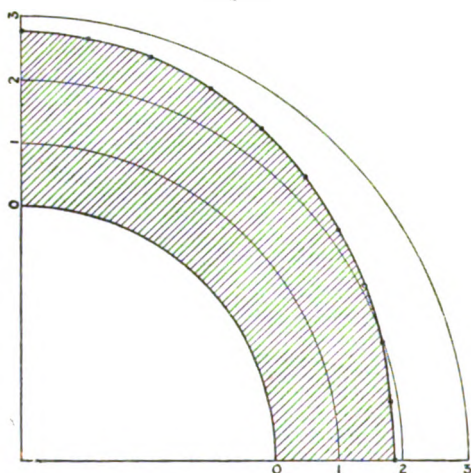
7. Systems which involve *three* principal stresses may be treated similarly; and since the effects of a flaw, in a homogeneous stress-system, are found to be unimportant except in its immediate neighbourhood, we may safely extend our solutions to any elastic system whatever, provided only that the dimensions of the flaw are so far restricted that no appreciable variation in the directions or magnitudes of the principal stresses occurs within a range of (say) three or four diameters from its centre.

For our present purpose it is sufficient to consider the special case of two principal stresses, equal in magnitude and opposite in sign. The results for this case may evidently be employed to investigate the effect of a small spherical flaw upon the stresses which occur in a twisted shaft; for the stress-system which would obtain in the absence of the flaw will here consist at any point of a simple *shear*, of calculable intensity  $S$ , and as such can be resolved into two normal stress-components,—a uniform tension of intensity  $S$

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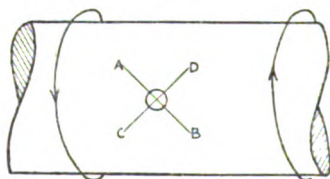
in one direction (making an angle of  $45^\circ$  with the axis of the shaft), and a uniform compression of equal intensity in a direction perpendicular to this. The effects of a spherical flaw on each component system will be of the nature illustrated in figs. 3-6, and the resultant tension on a plane which is perpendicular to the direction of the principal tension will be distributed, at the surface of the flaw, in the manner indicated in fig. 7. The stress is everywhere tensile, and varies slightly with position, its maximum value being of the order  $2.7 S$ .

Fig. 7.



The stress across a plane which is perpendicular to the direction of the principal *compression* will, of course, be similar in magnitude and distribution, but opposite in sign.

Fig. 8.



To sum up:—If a small spherical flaw exists in a shaft which is subjected to torsion, as shown diagrammatically in fig. 8 \*, then the stress at the surface of the flaw will range

The flaw is not necessarily situated near the surface of the shaft.

from a maximum tension of about 2.7 S at some point in the plane AB to a maximum compression of the same amount at some point in the plane CD. For points in other planes the stresses will have intermediate values, and detailed investigation shows that the amount of the increase at the surface of the flaw drops fairly quickly as we depart from the planes AB and CD.

*Propagation of a Crack in a Twisted Shaft.*

8. We may assume that the foregoing results will apply, without serious loss of accuracy, to cases in which the stresses are "alternating,"—i. e., where there is a danger of fracture as a result of fatigue. They are the more important in such cases, in that the power which a ductile material possesses of yielding plastically in regions where the stresses are excessive (thereby equalizing the load) is very much reduced when the stresses are periodic. A fatigue fracture, in fact, exhibits roughly the same characteristics as a fracture in a brittle material; and if in a crankshaft it originates out of a small flaw in the material, the foregoing considerations suggest that it will spread from the surface of the flaw, as a crack which follows the direction of that surface across which the principal stress is tensile.

Actual materials, as was remarked in § 1, are anisotropic, more especially as regards their resistance to elastic breakdown and to fatigue. At any given point in a crankshaft there will be one or more directions in which cracks will extend more readily than in others, and in general these directions will not coincide with the direction in which, on the foregoing theory, a crack would have extended in an isotropic material. It follows that the direction actually followed by the crack at any point will be a compromise between the direction of least resistance and the direction of greatest effect. But in the material as a whole, if the directions of greatest weakness are arranged at random, without definite orientation, we may still assert, speaking statistically, that the crack will follow the helicoidal surface across which the tensile stress has maximum values, although we shall not be surprised to find that the surface of the fracture exhibits facets which are inclined to its general direction.

Again, if a flaw of spherical shape, which possesses perfect symmetry, concentrates the tensile stresses upon planes of such definite orientation, it is to be expected that the crack will exhibit an even more pronounced tendency to follow a definite direction when once it has started; for the intense

curvature of the free surface at the edge of the crack will magnify to an enormous extent a tensile stress which acts perpendicularly to the general direction of the crack, but it will have practically no effect upon a tensile stress which acts parallel to that direction. Thus a crack which spreads in a direction of greatest weakness will tend in so doing to relieve the concentration of stress at its edge, if that direction differs widely from the direction of fracture which our theory would predict for an isotropic material; but if the two directions are more or less coincident, the concentration of stress will become intense. Similar considerations will apply, with greater or less effect, to any stress-system, and the general conclusion stated in §2 will hold, that *a fatigue fracture, once started, follows the surface on which the greatest principal tensile stress occurs.*

We may conclude, in regard to Prof. Jenkin's "spiral fracture," that when the surface of the fracture is inclined at an angle of approximately  $45^\circ$  to the axis of the shaft, it is attributable to fluctuating torsional stresses; whereas a sensible departure of the surface from this direction will indicate the existence of other contributory causes. In the same way, a fracture which followed a plane surface normal to the axis of the shaft would be diagnosed as due to fluctuations either of axial tension or of flexural action, and so on.

## Part II.—THE ORIGIN OF FATIGUE FRACTURES.

### *Application of the Theory to Laboratory Tests. Preliminary Experiments.*

9. The theory outlined in the preceding paragraphs affords an explanation of the paths which are followed by fatigue fractures once they have started, but it has no direct bearing on the question of their *origin*. On the supposition that the material was initially weakened by a small flaw or by a surface scratch, we have all the conditions which it requires in order to explain an observed "spiral fracture"; and in an example of the kind contemplated by Prof. Jenkin (where some cause of abnormal weakness must be assumed, to account for failure under loads which would ordinarily have been safe) the supposition seems permissible. But to explain the invariable occurrence of spiral fractures when specimens of certain materials are broken under alternating torsion in the laboratory, we must have recourse to some other hypothesis: either discontinuities of structure, equivalent to

ultramicroscopic flaws, must normally exist in these materials even when their quality would be generally regarded as "sound," or the test must have brought about local concentrations of stress which were sufficiently intense to overcome the cohesion of the material.

The first hypothesis has been advanced by A. A. Griffith, in an important paper\*, to explain the very low strength of brittle materials in relation to their theoretical "cohesion"; and the arguments by which he supports his theory are so convincing that recourse to the second hypothesis seems unnecessary, so far as brittle materials are concerned. But in the case of certain ductile materials torsional fatigue fractures commonly extend in circumferential or axial directions,—that is to say, along surfaces generally coincident with those of maximum shear and zero tension. On the basis of the first hypothesis, we must account for this different behaviour by assuming that *flaws of the kind contemplated in Griffith's theory of brittle substances do not normally exist in these ductile materials.*

10. To establish the validity of this explanation, it must be shown that ductility will not prevent the occurrence of helicoidal fractures in cases where a flaw is initially present. Torsional fatigue tests were accordingly undertaken on a series of hollow specimens (external diameter 0.400 in., internal diameter 0.313 in., length of parallel portion 1.2 in. and 0.8 in.) cut from two different steels, the carbon content being 0.27 per cent. and 0.65 per cent. respectively. The improved Stromeier machine† was employed, and the stress cycle was in every case symmetrical about a zero mean value; the ranges of stress which were required to produce fracture of the material are given in the appended table of mechanical properties.

Fractures typical of those obtained in the torsion tests are shown in fig. 9. The specimen numbered 1 was of 0.27 per cent. carbon steel, and fractured circumferentially after 300,000 reversals of a stress cycle ranging between  $\pm 8.0$  tons/sq. in.; but an exactly similar specimen (No. 2), in which an initial flaw was created by drilling a small hole (0.0125 in. diameter) radially through one side, gave the double helicoidal fracture shown in the photograph. Fracture occurred in this instance after 830,000 reversals of a stress-cycle ranging between

\* Phil. Trans. Roy. Soc. A, vol. 221, pp. 163–198 (1920).

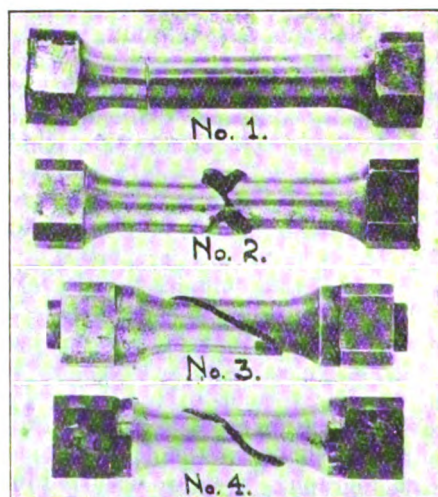
† Cf. H. J. Gough, 'Fatigue of Metals' (Scott, Greenwood & Sons, 1924, p. 40).

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 $\pm 7.0$  tons/sq.in. (calculated without regard to the effect of  
the hole).

TABLE I.—Mechanical Properties of 0.27 per cent.  
and 0.65 per cent. Carbon Steels.

		0.27 per cent. C. Steel.	0.65 per cent. C. Steel.
Static Tensile Tests.	Limit of Proportionality (tons/sq. in.)	20.6	19.2
	Yield Stress " "	21.0	28.0
	Ultimate Stress " "	31.2	53.0
	Percentage Elongation at Fracture (on a gauge length of 3.6 diams.) ...	44	19
Fatigue Tests.	Limiting Range of Stress in Reversed Bending Test (tons/sq. in.).....	$\pm 15.2$	$\pm 21.0$
	Limiting Range of Stress in Reversed Torsion Test (tons/sq. in.) .....	$\pm 7.3$	$\pm 10.5$

Fig. 9.



The propagation of the crack along *two* helicoidal surfaces  
concurrently is at first sight surprising. But it will be



realized that in the course of a complete cycle of alternating torsion each of the surfaces in turn is subjected to an intense concentration of tensile stress, while the other experiences a similar concentration of compressive stress ; thus the crack will extend along each surface during the particular half-cycle in which a tensile stress acts across that surface, but will merely be closed (without recovery of cohesion across the fractured surface) during the half-cycle in which the surface is subjected to compression. Fairly exact symmetry in the initial conditions is, of course, required for the occurrence of this phenomenon, in order that the second crack may be started before the first has extended appreciably : it frequently happens that only one surface of separation is formed, as in the case of the specimens numbered 3 and 4 in fig. 9, which were both cut from the harder (0.65 per cent. carbon) steel. The specimen numbered 3 was undrilled, and gave the typical helicoidal fracture after 204,300 reversals of a stress-cycle ranging between  $\pm 10.8$  tons/sq. in. The specimen numbered 4 was drilled in exactly the same way as No. 2, and broke after 100,000 reversals of a stress-cycle ranging between  $\pm 10.4$  tons/sq. in. (calculated without regard to the effect of the hole).

11. *In all cases, when a flaw was created by drilling and the specimen then subjected to alternating torsion, helicoidal fractures resulted.* The tests thus appeared to confirm the theory of the present paper, as regards the statistically isotropic materials for which it was propounded ; but it seemed desirable to investigate whether this isotropy could be so far destroyed by initial stressing as to make the fracture follow a circumferential or axial path in spite of the existence of a flaw. If, for example, a drilled specimen were given a large initial twist by the application of a steady couple, a sufficient degree of ductility would prevent the occurrence of a helicoidal fracture under this load ; yet it seemed possible that the large amount of slip involved on axial and circumferential surfaces might result in the formation of minute flaws, either within the crystals or (more probably) at the crystal boundaries, and thus leave the material, as it were, "perforated" along these surfaces : if so, the fracture resulting from an alternating torsion cycle might be expected to start at the drilled hole, but to extend through the "perforations" rather than along the helicoidal surface which otherwise would be its natural path.



*Further Experiments. The Effects of Initial Straining.*

12. To test these ideas, a more systematic series of experiments was initiated. Two steels—one “mild” and one “hard”—were selected, on which many tests of various kinds had already been conducted, and which were therefore known to fracture, when tested in the form of solid specimens under alternating torsion, in very consistent fashion,—the hard steel along helicoidal and the mild along axial or circumferential surfaces. The following table gives properties of these materials which had been obtained previously:—

TABLE II.—Analyses and Mechanical Properties  
of “A” and “B” Steels.

Steel.	“A” (0.13 per cent. C.)	“B” (0.65 per cent. C.)
Analysis .....	C    0.13 Si    0.18 Mn    0.70 S    0.042 P    0.046	C    0.65 Si    0.14 Mn    0.11 S    0.20 P    0.03
Heat Treatment .....	Normalized at 850° C.	As received (hot rolled).
Tensile Test Results:—		
Yield Stress .....	20.0 tons/inch.	28.0 tons/inch <sup>2</sup> .
Ultimate Strength .....	30.6    “    ”	53.0    “    ”
Elongation, per cent. (on length $l = 4 \sqrt{A}$ , where A = area of cross-section) .....	40.0	16.0
Contraction of Area, per cent. ....	71.7	31.8
Wöhler Fatigue Range	16.3 tons/inch <sup>2</sup> (on $250 \times 10^6$ reversals basis).	21.0 tons/inch <sup>2</sup> (on $20 \times 10^6$ reversals basis).
Haigh Machine Fatigue Range .....	13.8 tons/inch <sup>2</sup> (on $10^7$ reversals basis).	19.2 tons/inch <sup>2</sup> (on $10^7$ reversals basis).
Stroneyer Machine Fatigue Range .....	8.5 tons/inch <sup>2</sup> (on $10^7$ reversals basis).	10.5 tons/inch <sup>2</sup> (on $10^7$ reversals basis).
(Hollow specimens)		

Hollow specimens were employed, the dimensions being as follows:—

External Diameter of Specimen .....	0.400 in.
Internal Diameter of Specimen .....	0.313 in.
Length of Parallel portion of Specimen.	1.10 in.
Total Length of Specimen .....	2.70 in.

13. The scheme of the experiments included the following tests :—

- (a) Static torsion test (single-lever Buckton machine) : the torque-twist curve to fracture was determined. (One specimen of each material.)
- (b) The typical fracture under a range of reversed torsional stresses was determined. (One specimen of each material\*.)
- (c) A hole (0.013 in. diam.) was drilled through one side of the hollow specimen, and a fatigue fracture obtained. (Two specimens of each material.)
- (d) The material was subjected to four reversals of static overstrain ; a hole was then drilled (of the same size as before), and the specimen fractured in fatigue. (Two specimens of each material.)
- (e) The hole was drilled first, and the specimen subjected subsequently to four reversals of static overstrain, followed by a fatigue test to fracture. (Two specimens of each material.)

For the fatigue tests, the improved Stromeyer machine was employed. The ranges of torque applied (which in this machine are conditioned in some degree by the elastic behaviour of the specimen) are given in the following tabular summary of results :—

TABLE III.—Fatigue Tests on the Mild Steel “A” (fig. 10)†.

In the Static Torsion Test (a), the specimen (No. AVN5Q) yielded under a torque of 206 inch-lb. (shear stress at yield = 11.7 tons/inch<sup>2</sup>), and failed (by collapse, see fig. 10) under a torque of 400 inch-lb. (modulus of rupture = 22.7 tons/inch<sup>2</sup>). In the tests (d) and (e), the static overstrain (preliminary to the fatigue tests) was produced by a torque of  $\pm 250$  inch-lb. (shear stress =  $\pm 14.2$  tons/inch<sup>2</sup>).

Conditions of Test.	Specimen Number.	Range of Torque (inch-pounds).	Reversals to Fracture.
(b) .....	AVN5N	$\pm 16.0$ *	Less than 1,000,000 (Cut-out did not operate).
(c) .....	AVN5O AVN5P	$\pm 144$ $\pm 148$	Less than 650,000 (dto.) 244,400
(d) .....	AVN5U AVN5T	$\pm 144$ $\pm 148$	58,400 113,700
(e) ... ..	AVN5R AVN5S	$\pm 147$ $\pm 154$	521,000 298,000

\* Including tests made previously, the normal fracture was determined on six specimens of each material. The results were in all cases identical with those given in the tables and diagrams.

† The letters on the specimens in fig. 10 correspond with the final letters of the “Specimen Numbers” (column 2 of Table III).

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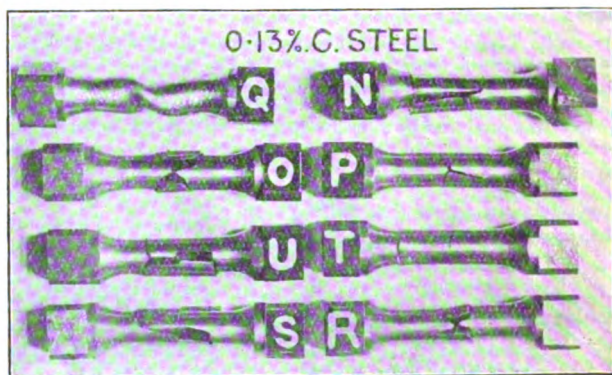
TABLE IV.—Fatigue Tests on the 0·65 per cent.  
C. Steel “B” (fig. 11)\*.

In the Static Torsion Test (*a*), the specimen (No. B.11.F. 2) yielded under a torque of 275 inch-lb. (shear stress at yield = 15·6 tons/inch<sup>2</sup>), and failed (by collapse, see fig. 11) at a torque of 700 inch-lb. (modulus of rupture = 39·8 tons/inch<sup>2</sup>). In the tests (*d*) and (*e*), the static overstrain (preliminary to the fatigue tests) was produced by four applications of a range of torque of  $\pm 375$  inch-lb. (shear stress =  $\pm 21\cdot3$  tons/inch<sup>2</sup>).

Conditions of Test.	Specimen Number.	Range of Torque (inch-pounds).	Reversals to Fracture.
( <i>b</i> ) .....	B.11.F.1.	$\pm 289$	94,300
( <i>c</i> ) .....	B.11.F.7.	$\pm 210$	507,800
	B.11.F.8.	$\pm 261$	12,000
( <i>d</i> ) .....	B.11.F.3.	$\pm 210$	68,200
	B.11.F.4.	$\pm 219$	9,400
( <i>e</i> ) .....	B.11.F.5.	$\pm 210$	55,100
	B.11.F.6.	$\pm 233$	6,700

14. The general appearance of the fractured specimens will be seen from the photographs of figs. 10 and 11 ; the

Fig. 10.



actual directions of the fractures are shown more clearly by fig. 12, in which the outer surface of the parallel portion of each fatigue specimen has been developed. Letters and numbers in this drawing conform with those of figs. 10 and 11 ; the developments have been arranged so that the point at

\* The numbers on the specimens in fig. 11 correspond with the final figures of the “Specimen Numbers” (column 2 of Table IV).

which fracture commenced appears at the centre of the developed area.

Fig. 11.

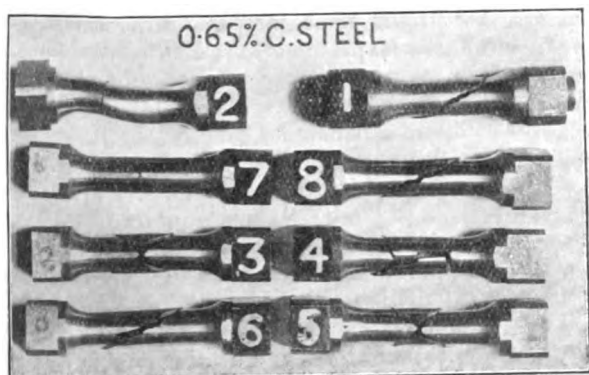
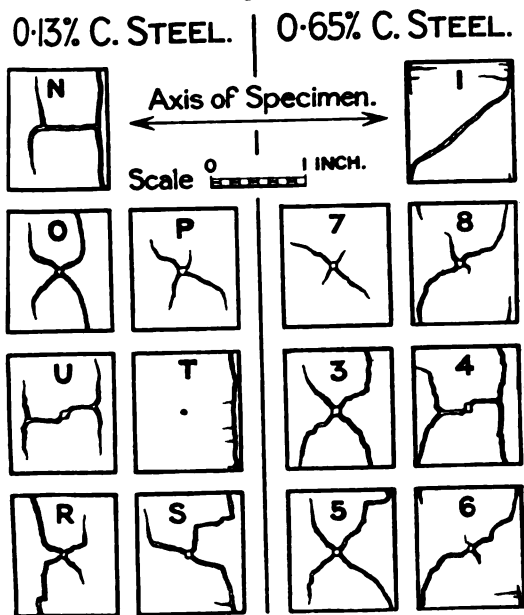


Fig. 12.



Considering the tests in the order given in § 13, we conclude from the type of failure which occurred in the static tests (a) that both materials possess a considerable measure

of "ductility"; this is also shown by the tensile test results given in Table II. On the other hand, the typical fractures obtained in the standard torsional fatigue tests (*b*) show that these two materials differ in their behaviour under alternating stresses in the same way as did the materials tested in the preliminary experiments (§ 10). Tests (*c*) on the drilled specimens confirm the conclusion of § 11, that a flaw (at all events, when its size is that of the drilled holes) invariably results in a helicoidal fracture of the statistically isotropic material under alternating torsional stresses.

Initial overstrain, applied to the specimens before drilling, is shown by tests (*d*) to have such important effects on the "A" material that one specimen (No. AVN5T, fig. 12) fractured circumferentially along a surface which did not pass through the drilled hole. In the "B" material also it has a perceptible tendency to make the fracture follow an axial or circumferential path, but the causes making for helicoidal fractures are here less definitely outweighed. Tests (*d*) indicate that the effect of overstrain is reduced when the hole is drilled first; but it is still perceptible.

### *General Conclusions.*

15. It has been remarked already (§ 9) that no light is thrown by the theory of Part I upon the *origin* of fatigue fractures; neither is it claimed that the experiments just described have gone far to supply an explanation. More and more it appears that the phenomena of fatigue in metals are intimately related with their molecular structure, and will not be explained by a mere elaboration of mechanical tests on the crystalline aggregate. But one fact may fairly be regarded as established by the present investigation,—that a flaw in statistically isotropic material inevitably results in the helicoidal type of fracture under alternating torsional stresses; and this being so, something may perhaps be learned from a study of the experimental fractures as indicators of the existence or non-existence of "flaws",—more especially if we can avoid reference to controversial questions which are involved in particular theories of breakdown and fatigue.

In a material like cast iron, which fractures along a helicoidal surface even when tested under static torsion, we may conceive, as in Griffith's theory \*, that "flaws" (*i. e.*, cavities large enough to be tractable by the mathematical theory of

\* *Loc. cit.*, pp. 179, 193.

Part I) are initially present, and that these, owing to its low ductility, produce local concentrations of stress which result in rupture of the material. So far as our experience goes, no other metal which is commonly employed in engineering behaves in this way: in the "B" steel of §§ 12-14, for example, the typical fracture under static torsion is illustrated by the specimen numbered 2 in fig. 11. The reason presumably is, not that the material in its normal condition has no flaws, but that high intensification of stress under static loading is prevented by its ductility; for the invariable occurrence of helicoidal fractures in the normal fatigue tests (*b*), where the ductility was less able to relieve the stress-concentration, indicates that flaws were certainly present at an early stage in the tests, and that they have had the result which our theory would predict.

This view is confirmed by the very distinct types of fracture obtained with the "A" and "B" steels in tests (*b*), which suggest that flaws were present in the "B" material, but not in "A". Thus we have indications of a difference between the "A" and "B" materials which is something more than a mere difference in respect of the property known as "ductility"; we may describe it by saying that the "A" material offers greater resistance to the formation of flaws in the course of manufacture or of mechanical treatment such as "cold-work,"—a quality which it is perhaps permissible to term "gumminess." No evidence is available, of course, from our mechanical tests to indicate whether surface tension is, in fact, a measure of the quality.

16. If in the "B" steel flaws were present initially, "perforation" of the material, which in § 11 was contemplated as a possible result of overstrain, might be expected to have a somewhat indefinite influence on the direction followed by a subsequent fatigue fracture; this we have seen (§ 14) to be the case. But it remains an open question whether the action of overstrain is, in fact, described by the notion of "perforation"; and even though this description were true of the "B," it would not necessarily be true of the "A" material. *The most significant result of the tests is the axial or circumferential direction followed by a normal fracture of the "A" steel\**; for it must be remembered that the crack has extended gradually, and according to the theory of Part I it should have an overwhelming tendency to follow a

\* Fractures following these directions are fairly typical of high-grade mild steel: mild steel of indifferent quality often gives a helicoidal fracture.

helicoidal path when once it has started. Thus it seems certain that the slipping on axial and circumferential surfaces, which occurs from the beginning of a fatigue test, has in some way destroyed the statistical isotropy of the material and caused these surfaces to become directions of special weakness; but it seems equally clear that the weakness must be due to a modification of the material rather than to the formation of flaws, since *the directions of special weakness must have been established by the time that the first flaw was formed*; and if this modification is the result of the to-and-fro slipping which occurred in tests (b), it is conceivable that the slipping which occurred in tests (d) under the initial static overstrain had a similar effect.

17. The general conclusion would appear to be, that the direction followed by a fatigue fracture, in a laboratory test of undrilled material, is influenced by two factors,—the tendency of a crack to intensify stress, and the tendency of slipping on any surface of the material to make this a direction of special weakness. The tendency of the crack has been shown, both by theory and experiment, to be development along surfaces of maximum *tension* (*i. e.*, in a torsion test, along helicoidal surfaces): the tendency of the slipping is to make the crack follow surfaces of maximum *shear*,—*i. e.*, surfaces inclined at  $45^\circ$  to the first. Either tendency may predominate under suitable circumstances, and the balance may be so nearly even, in special instances, that both effects are perceptible in turn. Thus it is frequently noticed, in testing specimens which increase in diameter towards their ends by a continuous transition curve, that a fracture which starts in an axial direction branches off into helicoidal paths as this curve is approached: presumably the explanation is, that the shear imposed by the initial overstrain decreases with the increase in diameter, so reducing the amount of the slipping, and hence the degree of weakness produced, in axial and circumferential directions; the “flaw effect” then predominates, and controls the subsequent path of the fracture.

Of the two conflicting factors just mentioned, the present paper, being in the main theoretical, really deals only with one,—the effect of flaws after their initiation. But in regard to the second,—the weakening effect upon the crystalline aggregate—it suggests two important conclusions: first, that the weakening is probably not described by the notion of “perforation,”—*i. e.*, that it is due to something other than the formation of large numbers of flaws along the

surfaces of maximum slip ; and secondly, that this other process, whatever it may be, is almost certainly a precursor of the fracture, and therefore predominant in importance for the problem of fatigue. The study of fractures is of value in the diagnosis of failures which have occurred in practice ; but the outstanding question in the general problem is the nature of the process (possibly a modification of molecular structure) whereby surfaces on which continued slipping has occurred are made directions of special weakness, although no discontinuity, such as is suggested by the term "flaw," is brought into existence.

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VII. *The Absorption of Hydrogen in Potassium Vapour Arcs.*  
By ROGERS D. RUSK, Ph.D., Ryerson Physical Laboratory,  
University of Chicago\*.

IT has been noted by Gehlhoff † and others that hydrogen is rapidly absorbed by hot potassium vapour when a high-tension electric discharge is passed through the vapour. In the following experiments the absorption was found to occur in a low voltage arc in which ionization currents were obtained between a coated platinum filament and an anode, through hot potassium vapour and hydrogen.

Hydrogen and potassium combine chemically to form potassium hydride ‡,  $\text{KH}$ , when they are heated together, and most probably the combination occurs in the presence of atomic hydrogen. The dissociation of hydrogen in an electric arc may be due to electron impacts, to thermal effects, or to the impacts of ions or excited atoms or molecules. If we take the heat of dissociation of a gram-molecule of hydrogen to be 84,000 calories, as given by Langmuir, the required energy per molecule is 3.6 volts. It might be suspected that direct electron impacts of this amount would produce dissociation, but Hughes § has made a very careful investigation and has found no trace of such dissociation due to impacts of less than 13 volts energy, and only slight dissociation below 16 volts. The question arises as to whether or not there is a critical potential for dissociation that would be indicated by the combination of H with K.

\* Communicated by Prof. A. J. Dempster.

† *Verh. d. Deutsche Phys. Ges.* xiii. p. 271 (1911).

‡ Moissan, *Compt. Rend.* cxxxiv. p. 71 (1902).

§ *Phil. Mag.* xli. p. 778 (1921).



Horton and Davies\* have found that the radiation at 11.9 volts is handed on to shielded electrodes by the molecules, while that at 12.9 volts is not. This, they suggest, indicates that the 12.9 volt radiation is due to dissociation of the molecules and resonance of the atoms. This would account for the lower limit of dissociation given by Hughes, except that the work of dissociation (12.9 volts—10.3 volts) comes out only 2.6 volts.

Hughes estimates that at 140 volts approximately every collision produces dissociation. The dissociation he obtained at 13 volts was very slight and approximately one-tenth that at 16 volts, so that at or near 16 volts a sharp increase in the absorption occurred. This would be in agreement with the interpretation that has been usually given to the 16 volt level, as the one at which dissociation plus ionization of one of the atoms occurs.

Olmstead†, in studying radiation and ionization effects, was able to assign definite critical potentials to molecular hydrogen, but without determining whether or not there was dissociation. Duffendack‡ found that the Balmer series appears at 16 volts, and this observation, which was confirmed by Horton and Davies, was taken to indicate dissociation plus ionization of one of the atoms.

The dissociation and formation of the charged atom probably occur, however, as a result of a secondary process. Dempster§ has shown by a positive ray analysis of the products of ionization that the presence or absence of hydrogen atoms and  $H_2$ , when hydrogen is ionized by electron impacts, is determined by the pressure in the tube. Hydrogen atoms were not formed at all as a primary effect with electrons of the velocity used, but only singly charged molecules. When the pressure was high enough to allow collisions to occur, charged atoms and the complex  $H_3$  were formed. Probably some of the molecules were thrown into excited states with energy sufficient to produce dissociation and ionization upon collision||. Smyth¶ has recently used similar methods in analysing the products of ionization produced by electrons of various voltages. In his paper in the 'Proceedings of the Royal Society,' he concluded that

\* *Ibid.* xlv. p. 872 (1923).

† *Phys. Rev.* xx. p. 613 (1922).

‡ *Phys. Rev.* xx. p. 665 (1922).

§ *Phil. Mag.* xxxi. p. 438 (1916); *Phys. Rev.* viii. p. 651 (1916).

|| J. Franck, *Ergebnisse der Exakte Naturwissenschaften*, ii. p. 107.

¶ *Proc. Roy. Soc.* 105 A, p. 119 (1923); *Jr. Frank. Inst.* cxviii. p. 795 (1924).

there were different critical minima potentials in hydrogen, 20.2 volts for the formation of charged hydrogen atoms and 16 volts for charged hydrogen molecules. Hogness and Lunn\* have also examined the products formed by low voltage electrons, and find values of 15.7 volts for the formation of the charged hydrogen molecule and 16.6 volts for the charged hydrogen atom. Recently Smyth† has ascribed his former result to an insufficient consideration of the effect of the gas-pressure on the products present, and finds that charged atoms as well as molecules may be present with electron impacts of about 16 volts. The slight difference in Hogness and Lunn's experiments may possibly be due to experimental uncertainties in the corrections applied.

That hydrogen may be dissociated by collisions with mercury atoms excited by 2537 Å. radiation, which is equivalent to an energy of 4.9 volts, has been shown by Franck and Cario‡, who illuminated a mixture of hydrogen and mercury vapour with the 2537 Å. radiation from a mercury arc, and observed the change in pressure of the hydrogen. The atomic hydrogen produced was condensed on cold walls, or oxidized by copper oxide, and the resultant water vapour frozen out. The same effect has been studied in a low voltage arc by Compton and Duffendack§. Since the energy of excitation of the mercury is just greater than the energy of dissociation of the hydrogen, the resultant dissociation is in agreement with the theory of Klein and Rosseland||. With hydrogen in potassium vapour such dissociation due to collisions with excited potassium atoms in the first excited state would not be expected, since the first resonance potential of potassium is 1.6 volts. However, as the ionizing potential of potassium is 4.3 volts, we might have the interchange of energy from some of the higher excited states to the hydrogen molecule.

### *Experimental.*

With pressures in the neighbourhood of one millimetre of mercury, absorption of hydrogen due to the arc was obtained at arc potentials above 16 volts and temperature up to 200° C. Absorption at slower rates was obtained in the presence of the hot filament alone, while at higher

\* Proc. Nat. Acad. Sc. x. p. 398 (1924).

† Phys. Rev. xxv. p. 452 (1925).

‡ Zeit. f. Phys. xi. p. 161 (1922).

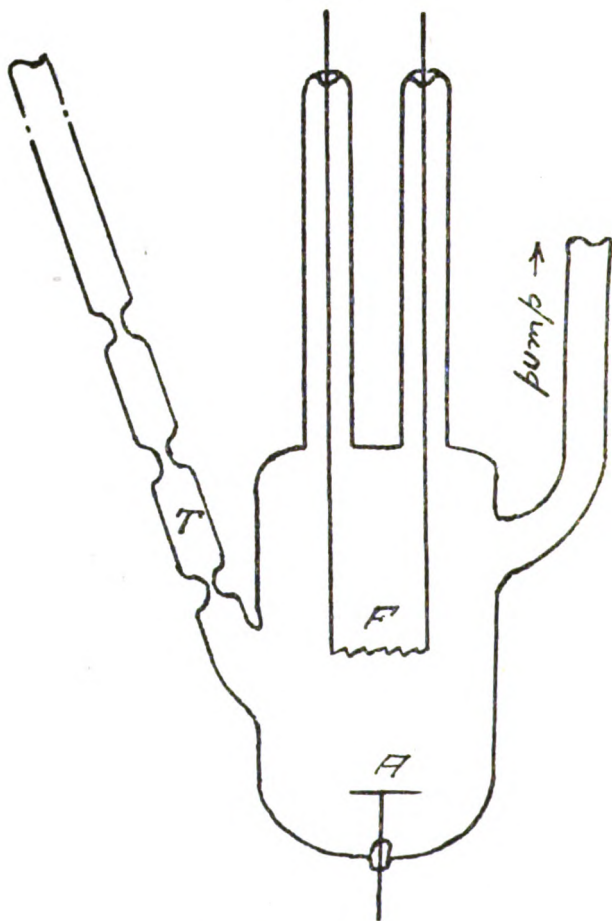
§ Phys. Rev. xxiii. p. 583 (1924).

|| Zeit. f. Phys. iv. p. 46 (1921).

temperatures and pressures absorption was obtained by simply heating the hydrogen and potassium together.

The experimental tube, one form of which is shown in

Fig. 1.



The Experimental Tube.

fig. 1, contained a coated platinum filament, <sup>a</sup>F, a nickel anode, A, and a side tube, T, with constrictions for filling with potassium. The rate of absorption of the hydrogen was obtained from observations of the change in pressure,

made in the usual manner with a McLeod gauge. A liquid air-trap took out water-vapour and mercury, and the system was evacuated by a mercury-vapour pump. A stop-cock enabled the experimental tube and McLeod gauge to be isolated from the rest of the system while a series of observations was being made.

Caution was observed in filling with potassium in order to have it as pure as possible. A coating on the surface of the potassium greatly reduced the absorption, and it was noticed that a straight chemical absorption occurred if any oxygen was present. Hence traces of air or water-vapour were particularly undesirable. The procedure was first to pump down the tube and bake out the residual gas at  $400^{\circ}\text{C}$ . The filament was out-gassed for several hours at a higher temperature than that at which it was to be normally run. The potassium was introduced into the filling-tube and partially distilled by repeated melting down and sealing off the residue *in vacuo* or in an atmosphere of hydrogen. The temperature of the tube was then controlled by a heating-coil placed around the tube. Pressures of the hydrogen were read every one, two, or three minutes, first with the arc and filament off, next for a few minutes with the arc off but with the filament on, and finally with the arc on.

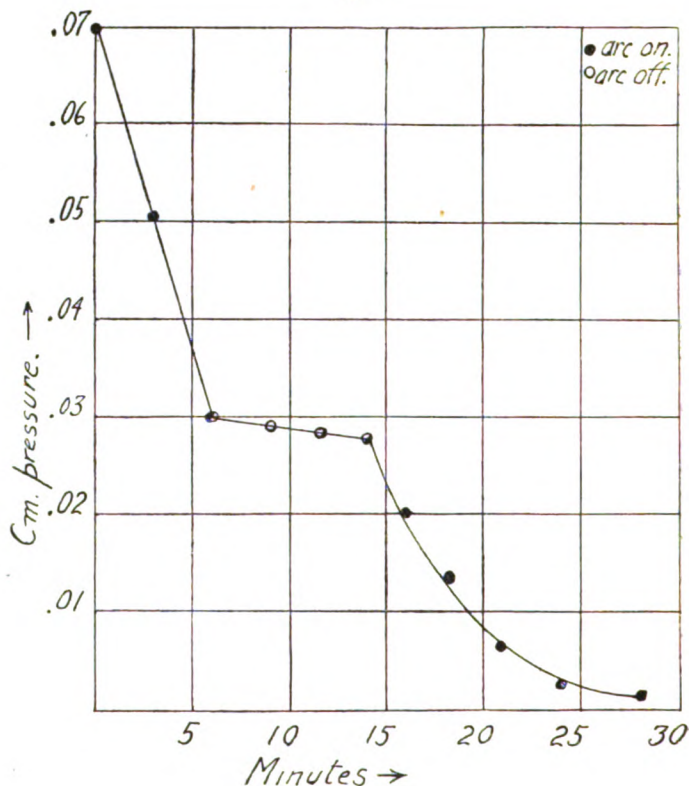
Arc currents up to 30 milliamperes were obtained, and the filament current was continually adjusted as the pressure went down in order to keep the filament temperature as nearly constant as possible. It was found that the absorption of the hydrogen due to the thermal effect of the filament was appreciable at temperatures above a very dark red, and increased rapidly with the temperature. Hence the filament was burned at as low a temperature as possible. In calculating rates of absorption, corrections were applied for the effect of the filament when it was not negligible. Any absorption on cold walls, as in the experiments of Hughes, and Franck and Cario, was of course not present, due to the high temperature of the tube.

On account of the experimental difficulties involved, it was found impossible to control all factors in such a way as to obtain exactly the same rate of absorption for successive experiments, though the results were in general qualitative agreement. The absorption of the hydrogen was usually accompanied by a characteristic violet colour of the arc, while at lower voltages a green colour predominated, and no absorption occurred.

*Data and Results.*

Figs. 2 and 3 give the observations in typical experiments. It is noted that the absorption is rapid at the start, and that sharp breaks occur in the curve where the arc was temporarily cut off. The smaller absorption here was due to the thermal effect of the hot filament. The study of a large

Fig. 2.



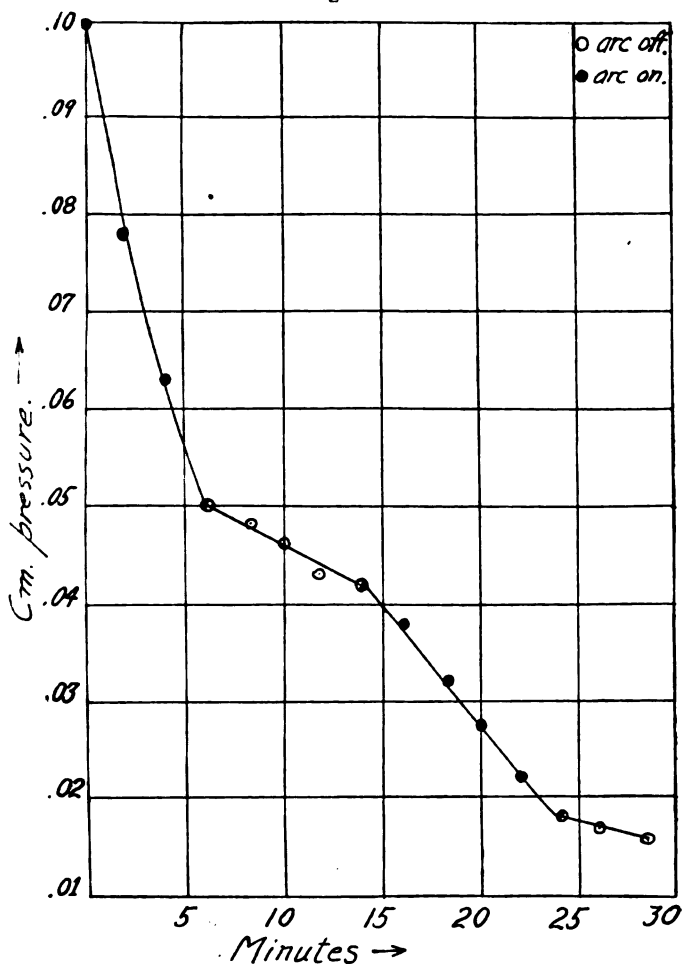
Typical Absorption-Curve, 190° C., 22 volts, 30 milliamperes.

number of such curves indicates that during the early part of each experiment the time rate of pressure change,  $\frac{dp}{dt}$ , was steady, and that it then decreased and finally decayed to the dissociation pressure of the potassium hydride.

The vapour-pressure of the potassium being small, in

comparison with the pressure of the hydrogen, the arcs were mainly arcs in hydrogen, except at extremely low pressures of the hydrogen. The striking voltage of the arc varied with the temperature, but the arc could always be struck at the ionization potential of the hydrogen.

Fig. 3.

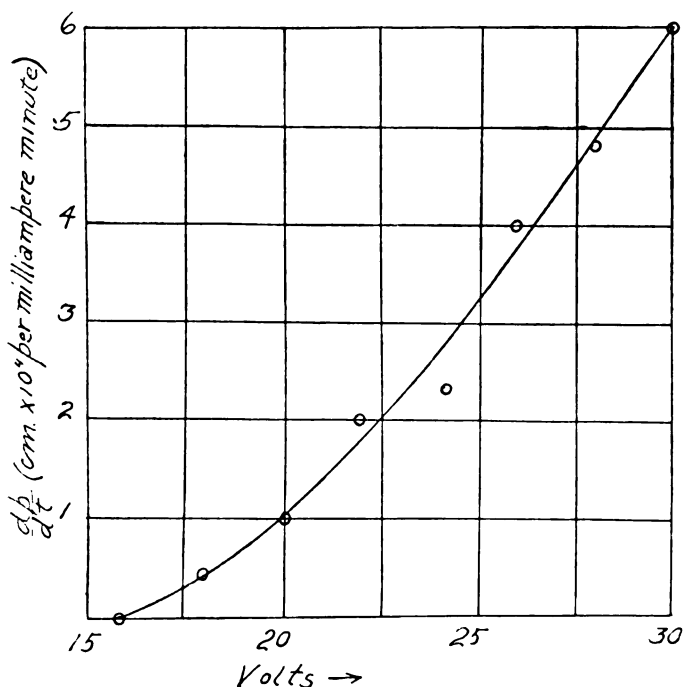


Typical Absorption-Curve, 190° C., 28 volts, 17.5 milliamperes.

With suitable vapour densities of the potassium it could be struck much lower, and was struck as low as 6 volts, but at the higher temperatures dissociation of the potassium

hydride was appreciable. Between 16 and 22 volts the arc was particularly unstable and sensitive to temperature fluctuations. As the absorption progressed the filament temperature would rise, resulting in greater electron emission and consequent lower voltage drop across the arc. Further absorption would reduce the ionization of the hydrogen and decrease the conductivity of the arc, resulting in an increased potential drop. The addition of a high resistance in the arc circuit helped to stabilize it.

Fig. 4.



Rates of Absorption at different Potentials.

Fig. 4 represents the results obtained with one tube, with which several series of observations were made. The ordinates give the rate of pressure decrease at the beginning of a series of observations for pressure in the neighbourhood of 1 mm. The rate of absorption increases rapidly with increasing voltage across the arc. Below 16 volts no absorption due to the action of the arc could be detected. Such an absorption, if present, was certainly less than

·0001 mm. per milliampere-minute, and was probably less than one-fifth that, as compared with ·002 mm. observed at 22 volts. Previously noted traces of absorption \* below 16 volts are attributed to the presence of a slight amount of oxide or dissociation by the filament.

Gehlhoff † mentions that "complete absorption" occurs at 190° C. At this temperature it was found that the absorption was most rapid, and dissociation of the potassium hydride was small. Keyes ‡ has measured actual dissociation pressures of potassium hydride between 215° C. and 415° C., and he gives the following formula for the dissociation pressure :—

$$\log p = -\frac{5850}{T} + 2.6 \log T + 3.895.$$

At 190° C. the dissociation pressure is ·001 cm. However, the absorption was obtained with lower temperatures, although at slower rate, as shown in fig. 5. Here the arc potential was 180 volts and the dissociation by the filament was negligible, due to the low temperature at which it was burned. It was found that the absorption was roughly proportional to the vapour density of the potassium. Dushman § gives an extrapolated value of  $6.84 \times 10^{-10}$  mm. for the dissociation pressure of KH at 27° C. To this theoretical residual pressure the hydrogen should be cleaned up at that temperature, but the rate of clean-up would be extremely slow.

The dissociation pressure of potassium hydride rises rapidly with increased temperature. It was found that an increase of the temperature of the tube, even while the arc was running, could be made to produce dissociation which, depending upon the amount of hydride present, would decrease the net absorption or cause a reversal with evolution of hydrogen and rising pressure. After absorption, and with the arc off, the hydrogen could be restored by raising the temperature of the tube.

For a comparative test, mercury-vapour was introduced into the arc with the hydrogen and potassium, and absorption at potentials below 16 volts was immediately observed, together with the appearance of the mercury lines in the arc. At 13 volts across the arc the absorption in the presence of the mercury was of the same magnitude as that at

\* Phys. Rev. xxi. p. 720 (1923).

† *Loc cit.*

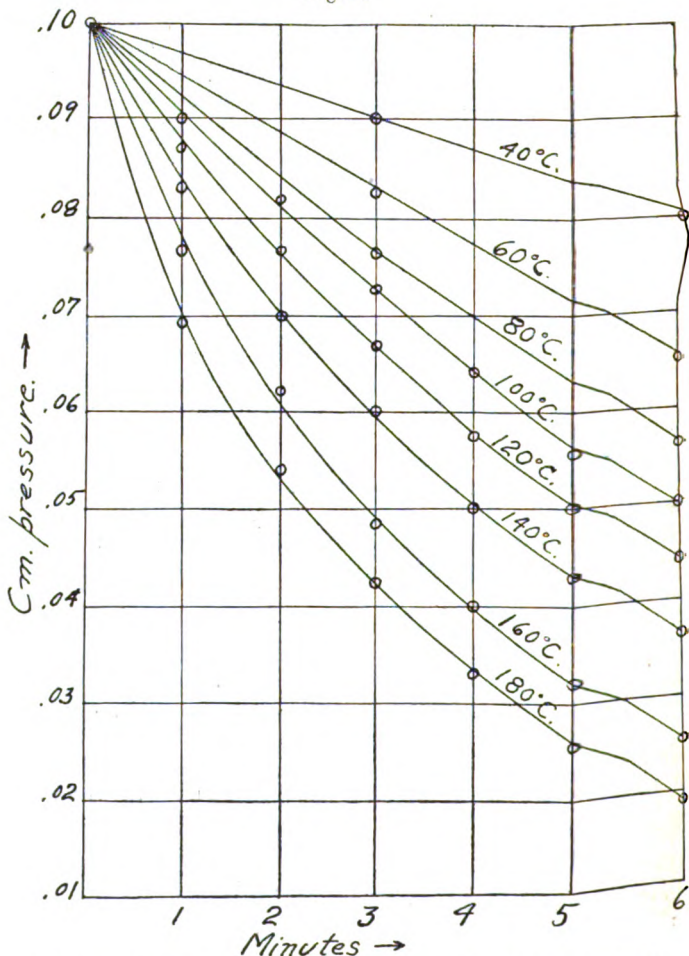
‡ J. Am. Chem. Soc. xxxiv. p. 779 (1912).

§ "High Vacua," General Electric Review.



22 volts without the mercury. This is direct evidence, as Franck and Cario \* have shown, that energy may be transferred to the hydrogen by means of collisions of the

Fig. 5.



Absorption at different Temperatures, 200 volts, 3 milliamperes.

“second type,” and that the energy of excitation of the mercury is capable of dissociating the hydrogen in a manner not possible by direct electron impacts of the same energy.

\* *Loc. cit.*

Using an ordinary glass tube without filament or electrodes, the absorption was measured at atmospheric pressure due to temperature alone. At  $300^{\circ}\text{C}$ . the absorption was  $\cdot 2$  c.c. per hour, and at  $375^{\circ}\text{C}$ . it was  $4\cdot 8$  c.c. per hour. Thus it appeared that the phenomena of the absorption produced in the arc could be reproduced, in effect at least, without the arc by sufficiently raising the temperature, an increased pressure of the hydrogen, of course, being necessary on account of the increased dissociation pressure of the potassium hydride.

### *Discussion and Conclusions.*

The absorption in the arc is evidently due to some active type of hydrogen which is not formed at less than 16 volts. Ionized potassium does not unite with molecular hydrogen, otherwise absorption would have occurred at  $4\cdot 3$  volts, the ionization potential of the potassium.

The active form of hydrogen present in the arc may be the charged hydrogen molecule, which might combine directly with a K-atom, freeing one of the H-atoms. But from experiments discussed in the introduction, it seems more probable that hydrogen atoms are formed as the result of a secondary process whenever charged hydrogen molecules are present. We may then suppose the combination to take place between potassium atoms and hydrogen atoms. On this view 16 volts is the lower limit at which dissociation of the hydrogen occurs.

The negative chemical characteristics of atomic hydrogen are well known. Bardwell\* has shown that hydrogen, in combination with potassium, behaves as a halogen and upon being electrolysed appears at the anode carrying a negative charge. When in union with the potassium atom, the valence electron of the latter doubtless goes to complete, in the hydrogen, the group of two electrons common to the more stable helium form. There is little doubt but that atomic hydrogen, if present in the arc below 16 volts, would readily unite with the potassium.

An upper limit for the rate of absorption in the arc due to the presence of molecular hydrogen ions may be obtained if we assume that all the current is carried by the electrons, and that each electron removed from the arc leaves a positive ion behind. It may be assumed that this positive ion gives rise to an atom which is absorbed by the potassium. At the pressures involved, the fraction of current actually carried

\* J. Am. Chem. Soc. xlv. p. 2499 (1922).

by the positives must be relatively small. With one milliampere of current through the arc,  $ne = 0.001$  in C.G.S. units, whence  $n = 6.3 \times 10^{16}$ . On the above assumption,  $n$  positive molecular ions per second are formed in the arc, and if each gives rise to an atom which is absorbed, or if the molecular ions themselves react with the potassium, then  $n$  atoms of hydrogen would disappear per second, or half that number ( $3.15 \times 10^{16}$ ) of molecules would disappear per second.

At 22 volts the observed number of hydrogen molecules disappearing per second per milliamperere of current was  $0.21 \times 10^{16}$ , which is one-fifteenth of the above upper limit. This may be taken to indicate that the molecular ions do not react as fast as they are formed, and that more probably only the atoms formed by a secondary process are absorbed. The figures would then indicate the effectiveness of the secondary process.

The steady rate of change of pressure,  $\frac{dp}{dt}$ , of the hydrogen which was observed at the start of each run would be expected if the vapour density of the potassium were constant, and if the arc furnished active hydrogen at a constant rate. The absorption was found to be proportional to the current through the arc, except in the case of very intense arcs, in which case there was some evidence of more rapid absorption, which may have been due in part to a higher effective temperature in the arc itself.

If we consider the absorption of hydrogen at high temperatures due to heat alone, the question arises as to whether it is an ordinary chemical reaction between the potassium and molecular hydrogen, or whether it may not be due to atomic hydrogen existing in equilibrium with the latter. The determination of so small an amount of dissociation cannot be exact, but by using Nernst's equation of the reaction isobar given below, the per cent. of dissociation at various temperatures and pressures may be calculated, where  $x$  is the fraction of monatomic molecules present.

$$\log \frac{x^2}{1-x^2} P = \frac{-Q_0}{4.571.1} + 1.75 \log T - \frac{\beta}{4.571} T + \Sigma \nu c^*.$$

At  $300^\circ \text{C}$ . and 76 cm. the per cent. of dissociation is, by the formula,  $1.75 \times 10^{-11}$ . Such a value is a somewhat

\* Ehrenfest and Trkal, *K. Akad. Amsterdam, Proc.* xxiii. 1, p. 162 (1920).

extreme extrapolation of the formula, and yet comes surprisingly close to accounting for the observed absorption. If the number of hydrogen molecules in 150 c.c. at  $300^{\circ}\text{C}$ ., 76 cm. be taken as  $1.84 \times 10^{21}$ , the number which are monatomic is seen to be  $3.42 \times 10^8$ . On the simple kinetic theory each molecule experiences  $7.77 \times 10^9$  collisions per sec. Hence all the hydrogen atoms make  $2.66 \times 10^{18}$  collisions per sec.,

of which the fraction  $\frac{.00497}{76}$ , or  $1.74 \times 10^{14}$ , is with potassium atoms, the vapour pressure of the potassium being .00497 cm., from the work of Keyes\*. Assuming that combination occurs at each collision, this would account for the removal of  $.87 \times 10^{14}$  hydrogen molecules per sec., which was about one-sixteenth of the observed rate. If the absorption is due to dissociated hydrogen these figures would indicate the probable magnitude of the dissociation. It is interesting to note that the above value for the dissociation by Nernst's formula is in striking contrast to that given by Langmuir†. The value taken from his table for the partial pressure of dissociated hydrogen, at  $500^{\circ}\text{K}$ . and atmospheric pressure, being  $1.7 \times 10^{-25}$ .

In conclusion, it was found that active hydrogen capable of combining with potassium is found in low voltage arcs above 16 volts; that the atomic form is probably atomic; that the dissociation is most probably due to secondary collisions; and that this dissociation does not occur below 16 volts.

The writer wishes in particular to thank Prof. A. J. Dempster, who suggested the problem, for his continued interest and advice.

VIII. *The Adsorption of Gases by Activated Charcoal at Very Low Pressures.*—I. *At Air Temperature.* By H. ROWE, B.Sc., Demonstrator in Physics, University College of the South-West of England, Exeter ‡.

### 1. INTRODUCTION.

**A**LTHOUGH much research has been made on the occlusion and retaining of gases and vapours by different substances, the intermingling phenomena which constitute sorption have not been experimentally identified, but in general there are three actions.

\* *Loc. cit.*

† J. Am. Chem. Soc. xxxiv. p. 877 (1912).

‡ Communicated by Prof. F. H. Newman, D.Sc., A.R.C.Sc.

1. Absorption. This is true solution in a solid and obeys Fick's law of diffusion, which requires that it should commence with a very high velocity for the first few moments, but fall off rapidly with time and, theoretically, should require an infinite period for perfect equilibrium to be attained. The action is accelerated by a rise in temperature.

2. Adsorption. This effect is condensation on a surface, and is practically instantaneous. Any time-lag which occurs is explained at present by the interval required for the dissipation of the heat evolved, or by the comparative inaccessibility of the surface on which condensation occurs. Adsorption decreases rapidly with rise in temperature, and it is conditioned by the surface extent, which in the case of metals is small. It is essentially a surface-tension phenomenon, and is sometimes influenced by electro-capillary effects.

3. Chemical reactions. These occur frequently in sorption processes, and may be of decisive importance, *e.g.* the behaviour of catalysts. Where pure chemical compounds are formed, each exhibits a definite decomposition pressure, below which the compound is not produced, and at which formation is complete. Chemical reactions are often present in the most varied phenomena, particularly as such reactions proceed vigorously in surface films, as well as in solid solution.

In 1909 Freundlich\* suggested that the relation between the pressure  $p$  and the quantity of gas  $q$  absorbed might be represented by an equation of the form

$$q = kp^{\frac{1}{n}}.$$

For low pressures or high temperatures, where the quantities adsorbed are small, the value of  $\frac{1}{n}$  approaches unity, while at high pressures and low temperatures it often becomes as small as 0.1. These values have been verified experimentally by Claude† and Titoff‡. They found that in the case of hydrogen  $\frac{1}{n}$  is approximately equal to unity at all pressures and temperatures. On the other hand, in the case of nitrogen and carbon dioxide  $\frac{1}{n}$  decreases rapidly as the pressure and

\* 'Kapillarchemie,' Leipzig (1909).

† *Comp. Rend.* vol. clviii. p. 881 (1914).

‡ *Zeits. Phys. Chem.* vol. lxxiv. p. 641 (1910).

temperature both increase. On the whole the relation does not agree with experimental observations over large ranges of pressures.

Quite recently A. M. Williams\* from the kinetic theory of gases has derived relations between the pressure, the quantity of gas adsorbed, and the temperature, which may be expressed by

$$\log q \cdot \frac{R.T.}{p} = B + \frac{A}{T}$$

and

$$\log q \cdot \frac{R.T.}{p} = A_0 - A_1 q.$$

The latter, representing the adsorption isotherm, may also be written in the form

$$\frac{q}{p} = K e^{-A_1 q}$$

where  $A_0$ ,  $A_1$ , and  $K$  are constants at any given temperature. It will be observed that for small values of  $q$ , i. e. for small amounts of adsorption, the exponential term is practically unity, so that at low pressures and high temperatures the latter equation reduces to the simple form

$$q = kp.$$

These equations are found to agree well with the experimental results obtained by Claude and Titoff, and also with those of Miss I. F. Homfray†.

According to Langmuir‡ adsorption is the result of a kinetic equilibrium between the rate of condensation and that of evaporation. On this basis the quantitative form of the adsorption isotherm depends on the nature of the mechanism of both condensation and evaporation. Using these conceptions of surface actions, Henry§ has developed a theory which he states applies to all cases where the adsorbent only contains not more than 30 per cent. of the saturation value of the adsorbate. The type of equation obtained is similar to that of Williams, and is

$$\log \frac{\alpha}{p} = \log A - A_1 \alpha.$$

where  $\alpha$  is the number of gram molecules adsorbed at the

\* Proc. Roy. Soc. (Edin.) vol. xxxix. p. 49 (1919); Proc. Roy. Soc. (Lond.), A, vol. xvi. p. 287 (1919).

† Zeits. Phys. Chem. vol. lxxiv. p. 129 (1910).

‡ Journ. Amer. Chem. Soc. vol. xl. p. 1361 (1918).

§ Phil. Mag. vol. xlv. p. p. 689 (1922).

pressure  $p$ ; or, reducing the above equation to cubic centimetres of gas at N.T.P., we have

$$\log \frac{q}{p} = A_0 - A_1 q.$$

Most of the investigations on adsorption phenomena have been carried out at pressures above 1 mm. \* and at liquid-air temperature, and little is known about adsorption at low pressures and higher temperatures, so that the formula quoted above cannot be compared with experimental results. Claude †, however, has measured the adsorption of various gases at pressures below  $10^{-3}$  mm.

From the known adsorptive capacity of an absorbent at higher pressures and low temperatures, it is not possible to predict with certainty the behaviour at low pressures and higher temperatures, since in the former case, where most gases are near their condensation state, the attraction between molecules of the gas is greater than the molecular attraction between the gas molecules and those at the surface of the solid. The contrary is true, however, at very low pressures, and more especially at higher temperatures.

The amount of gas which charcoal adsorbs and retains varies greatly with the equilibrium pressure; and since the function of charcoal in producing high vacua is the retention within it of gas molecules, it is the adsorption at low pressures which is important. Owing to the difference between the characteristics of adsorption at high and low pressures, it is impossible to predict the rate of adsorption in high vacua, and data given at ordinary pressures bear no relation to the retentivity of the substances at low pressures.

As a study of adsorption phenomena at very low pressures is likely to yield important results concerning the nature of chemical and physical action, a detailed study of the amounts of various gases adsorbed by activated coconut charcoal within the pressure range  $10^{-4}$  to  $10^{-1}$  mm. and at air temperature was made, and empirical relations between the pressure and the volume so adsorbed deduced.

## 2. Experimental Arrangement.

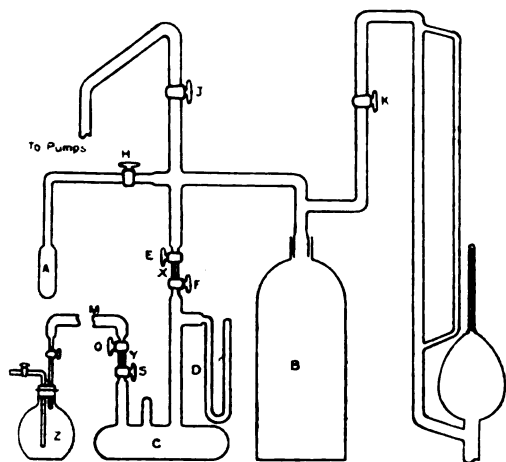
The apparatus used is shown in fig. 1, and consisted essentially of a bulb A containing the activated coconut charcoal which, by means of a tap H, communicated with a large volume B. C, a drying bulb containing phosphorus

\* Pressures are expressed in mm. of mercury.

† *Loc. cit.*

pentoxide, was used as a small reservoir, and X and Y were known volumes enclosed between taps. These volumes had been carefully calibrated previously. A sealed-limb mercury manometer D gave an indication of the pressure and hence the amount of gas in the reservoir C. The whole system could be evacuated by means of a Volmer mercury diffusion pump supported by a Cenco-Hyvac oil-pump. All pressures on the high vacuum side of the apparatus were read on a 500 c.c. McLeod gauge, which, having received continuous and prolonged heat treatment and having been in constant use for a considerable time, read consistently and accurately.

Fig. 1.



The gauge was sensitive down to  $10^{-5}$  mm., but the mercury pump when in action exhausted the whole system to a pressure not readable on the gauge. The volume enclosed between the taps J, H, E and the mercury in the McLeod gauge is termed the high vacuum side of the apparatus in the experiments described.

The whole system was evacuated without any charcoal in A to less than  $10^{-5}$  mm., and maintained at this degree of vacuum for several days, the pumps working continuously to remove gases and vapours from the glass walls. After all the gases and vapours had been removed, as indicated by no increase in pressure during an interval of 48 hours while the pumps were shut off, tap F was closed, and by admitting known volumes of dry air from Y into C, the latter was filled with dry air at about 50 mm. pressure.



To determine the volume  $V$  of the high vacuum side with which the charcoal tube communicated in all subsequent adsorption readings, the taps J, E, F being closed and H and K open, the pressure of any gas in the system was measured on the McLeod gauge. A known volume  $v$  of air at a pressure  $p$  indicated by the manometer D was then admitted by opening F, then closing it and opening the tap E. The final pressure after admitting the gas was noted on the gauge, and from these readings the volume  $V$  could be calculated.

Let

$p_1$  = original pressure,

$p_2$  = final pressure.

Then

$$p_2(V + v) = p_1 V + pv,$$

$$i.e. \quad V = v \frac{(p - p_2)}{p_2 - p_1}.$$

$p$  is of the order of several millimetres and  $p_2$  is of the order  $10^{-3}$  mm., so that approximately

$$V = \frac{pv}{p_2 - p_1}.$$

This process repeated about 50 times gave the average value of  $v$ , which was 3160 c.c.

The volume of the reservoir C was determined in a similar manner, known volumes of air at atmospheric pressure being admitted from Y and the resulting pressures on the mercury manometer D being measured. This volume was 112 c.c. It was necessary to keep the pressure in the bulb C fairly low, otherwise admitting a single volume of gas from X into the high vacuum side caused too great a change in the pressure as measured by the McLeod gauge.

The coconut charcoal used had been activated by the steam process, but before use it was reactivated by the "air oxidation" treatment. This was carried out by placing a shallow layer in a silica tube open at both ends and having an electric heating coil wound round it. The charcoal was heated to  $450^\circ\text{C}$ . for half-an-hour and air blown over its surface from time to time. The final sample was 8-10 mesh, hard and glossy and of bulk density 0.69.

A known weight of freshly reactivated charcoal was then placed in the bulb A, and the latter sealed to the main apparatus. The charcoal was completely outgassed by heating to  $450^\circ\text{C}$ . for 6 hours with the pumps working

continuously to remove any liberated gases. The charcoal was tested for complete outgassing by allowing it to cool, the tap H being closed, and the system at a pressure less than  $10^{-5}$  mm. The charcoal was then reheated to  $450^{\circ}\text{C}$ . for half-an-hour with H open, the pumps being shut off, and if no increase in pressure resulted it could be safely assumed that outgassing was complete. It was found extremely important to ensure that all of the gas had been eliminated, as the amounts of gas adsorbed at the low pressures used in the experiments were very small, and any residual gas produced inconsistent results.

The actual adsorption of the various gases was measured in the following manner. The bulb Z containing the gas to be used was sealed to M, and the whole of the apparatus exhausted to a pressure below  $10^{-5}$  mm. Taps E and F were then closed, and gas from Z admitted to C by alternately opening and closing the taps O and S. In this way the gas-pressure in C was raised to any convenient value.

Tap F was then opened so that a small volume of gas could be trapped between taps E and F. This volume was then admitted to the high vacuum side, tap H remaining closed during the operation. After 15 minutes the pressure of the gas was read on the gauge and noted. H was then opened and the gas admitted to the charcoal. When equilibrium conditions had been attained in the system the pressure was again noted, and from the initial and final pressures and the volume of the apparatus the amount of gas adsorbed by the charcoal was determined.

The tap H was again closed and the procedure described above repeated, the total quantity of gas adsorbed at the new equilibrium pressure being given by the summation of the previous amounts adsorbed while the pressure was changing from its initial to its final values. As the gases in the apparatus and in the charcoal are in equilibrium, it may be assumed that this sum is the amount of gas that would be adsorbed at the final pressure if the adsorption had occurred at one and the same time.

This process was repeated until the pressure-range  $10^{-5}$  to  $10^{-1}$  mm.—the limits of the gauge—had been covered. At the lower limit of this range one volume of gas admitted from EF caused a considerable change in the equilibrium pressure, but at  $10^{-1}$  mm. about five amounts of gas from EF were necessary to cause an appreciable change in the equilibrium pressure as read on the McLeod gauge.

A correction was made for the volume of the charcoal bulb and the connecting tubing to H ; this correction was

negligible when relatively large adsorptions took place, as with oxygen, but finite with small adsorptions as in the case of nitrogen. The air temperature was read at one hour intervals and the average value noted.

Let  $V$  = volume in c.c. of the high vacuum side,  
 $p_1$  = original pressure in high vacuum side,  
 $p_2$  = final pressure.

Then the volume in c.c. of the gas, at 1 mm. pressure and room temperature, adsorbed by the charcoal is given by

$$V(p_1 - p_2).$$

The same sample of charcoal was used for carbon dioxide, nitrogen, and oxygen, but was replaced by a fresh quantity for carbon monoxide, owing to the fact that it was impossible to remove all the oxygen, previously adsorbed, from the charcoal. This second sample was treated in an exactly similar manner to the first. The quality of the first sample, as an adsorbent, improved after several "gassings" and "outgassings." This phenomenon is well known and has been investigated by Lemon\*. It is one of the chief difficulties encountered when activated charcoal is used as a medium for the investigation of adsorption processes. Other substances, such as glass, wool, or mica, show varying adsorptive powers according to their previous treatment, but in no case is the discrepancy between the results of various experimenters more marked than with charcoal.

### 3. EXPERIMENTAL RESULTS.

#### a. Carbon Dioxide.

The gas was prepared by the action of pure hydrochloric acid on freshly-boiled air-free marble in a Wolff bottle, and after passing over calcium chloride and phosphorus pentoxide, to remove the excess of water-vapour, it entered a small bulb Z with taps on the inlet and outlet tubes. A rapid stream of carbon dioxide was passed through the bulb for 2 hours, before closing the taps, to ensure the complete removal of atmospheric gases. The reservoir C was then charged from this bulb as described previously, the pressure of the gas in C being about 60 mm.

\* *Phys. Rev.* vol. xiv. p. 282 (1919).

It was noted that at the low pressures employed carbon dioxide required a considerable time to attain equilibrium; comparatively rapid adsorption took place for the first 30 minutes, but was followed by slow adsorption during the succeeding 24 hours, and in some experiments continued for 3 days. Most of the gas was adsorbed during the first stage, and the slow adsorption that followed did not materially affect the volume adsorbed, but the final pressure attained depended on the time during which the gas was in contact with the charcoal. This time-effect was not observed below  $0.75 \times 10^{-3}$  mm. The effect has been studied, and the results obtained will be described in another paper.

During outgassing the last traces of carbon dioxide were removed with difficulty, and it was necessary to maintain the charcoal at  $450^{\circ}\text{C}$ . for 18 hours, the pumps maintaining the pressure below  $10^{-4}$  mm. before it was entirely eliminated.

The results obtained with carbon dioxide are shown in Table I., the volumes absorbed per gram of charcoal being given in c.c. measured at 1 mm. and  $15^{\circ}\text{C}$ . During the whole of the experiments on carbon dioxide the temperatures never varied more than  $\pm 1^{\circ}\text{C}$ . from  $15^{\circ}\text{C}$ . In the third

column, values of  $\log_{10} \frac{\alpha}{P}$  are given, where  $\alpha$  is the volume adsorbed per gram quoted at N.T.P., and  $P$  is the pressure in cm. of mercury.

TABLE I.

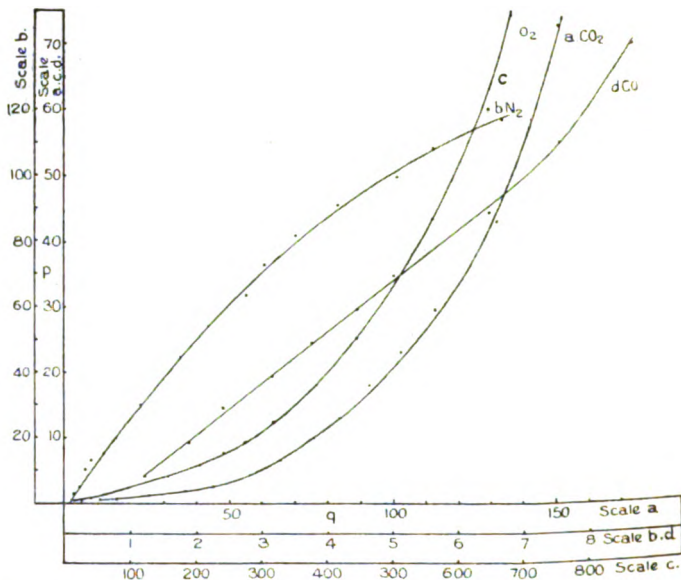
Adsorption of Carbon Dioxide at  $15^{\circ}\text{C}$ .

$P$ .	$q$ .	$\log_{10} \frac{\alpha}{P}$ .
$0.326 \times 10^{-3}$ mm.	5.165	2.2958
0.508	10.54	2.4129
0.729	15.44	2.4219
1.164	25.21	2.4309
2.515	45.17	2.3504
4.250	58.10	2.2166
6.378	65.63	2.1085
9.989	75.48	1.9743
17.85	92.70	1.8115
29.37	112.5	1.6791
42.78	131.2	1.5828
58.47	141.8	1.4808
73.02	150.5	1.4101

The graphical relation between  $p$  and  $q$  is shown in fig. 2, curve (a). At very low pressures, *i. e.* below  $1.5 \times 10^{-3}$  mm., the relation is linear and may be represented by

$$q = kp.$$

Fig. 2.



The results below  $3 \times 10^{-3}$  mm. are given on a larger scale in fig. 3, curve (a). The curve does not pass through the origin, but cuts the  $p$  axis at  $1.5 \times 10^{-4}$  mm. The continuity of the curve from the lowest to the highest pressures used indicates the absence of chemical action during adsorption, and is characteristic of a continuous series of solid solutions.

The adsorption equation

$$\alpha = kP^{\frac{1}{n}}.$$

may be written in the form

$$\log \alpha = \log k + \frac{1}{n} \log P,$$

and fig. 4, curve (a), shows the relation between  $\log_{10} \alpha$  and  $\log_{10} P$ . At first the curve is continuous, and its slope, *i. e.* the value of  $n$ , gradually increases. Above  $2.5 \times 10^{-3}$  mm. there is a linear relation between these quantities,  $n$  being constant and equal to  $\frac{1}{0.358}$ .

Fig. 3.

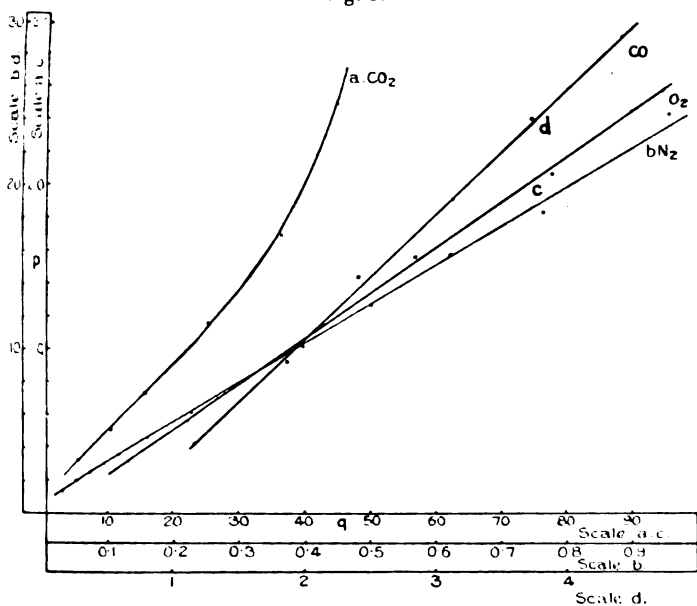
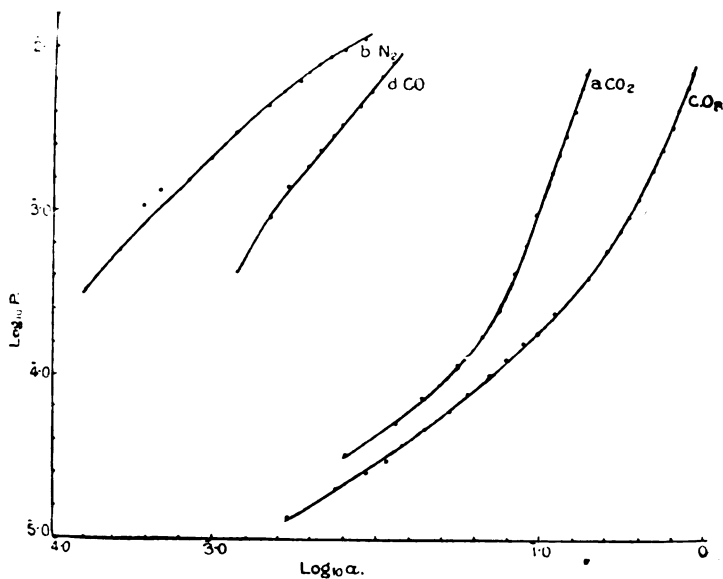


Fig. 4.



The values of  $\frac{1}{n}$  have been determined for various pressures and are shown in Table II.

TABLE II.

Values of  $\frac{1}{n}$  for carbon dioxide in the equation  $\alpha = kP^{\frac{1}{n}}$ .

Mean Pressure.	$0.417 \times 10^{-3}$ mm.	$0.836 \times 10^{-3}$ mm.	$1.455 \times 10^{-3}$ mm.	$2.130 \times 10^{-3}$ mm.
$\frac{1}{n}$ .. . . . . .	1.61	1.05	0.911	0.591

This decrease of  $\frac{1}{n}$  with increase in equilibrium pressure is in agreement with the conclusions of Claude \* and Titoff †, who found that  $\frac{1}{n}$  decreased rapidly with increasing pressure.

Considering the relation between  $\alpha$  and  $P$  proposed by Williams ‡ and Henry §, and plotting  $\log_{10} \frac{\alpha}{P}$  against  $\alpha$  || in fig. 5, curve (u), it is found that there is a linear relation between these quantities only at pressures above  $1.75 \times 10^{-3}$  mm. As the pressure increases from the lowest values  $\log \frac{\alpha}{P}$  increases with  $\alpha$ , then becomes constant, and finally decreases uniformly. The values of  $A_0$  and  $A_1$  in the equation

$$\log \frac{\alpha}{P} = A_0 - A_1 \alpha,$$

as determined from the graph, are

$$A_0 = 2.788 ; A_1 = 8.578.$$

These results show that below  $1.5 \times 10^{-3}$  mm. there is a

\* *Comp. Rend.* vol. clviii. p. 861 (1914).

*Zeits. Phys. Chem.* vol. lxxiv. p. 641 (1910).

† *Proc. Roy. Soc. (Lond.) A*, vol. xcvi. p. 287 (1919).

§ *Phil. Mag.* vol. xlv. p. 689 (1922).

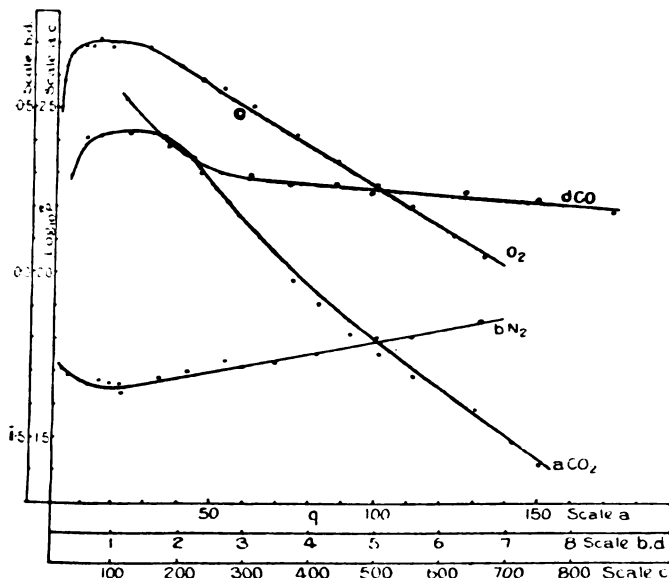
|| More convenient to plot  $\log_{10} \frac{\alpha}{P}$  and  $q$ .

linear relation between  $P$  and  $\alpha$ , and above this pressure the relationship may be represented by either

$$\alpha = kP^{\frac{1}{n}}$$

or  $\log_{10} \frac{\alpha}{P} = A_0 - A_1 \alpha.$

Fig. 5.



### b. Nitrogen.

The nitrogen used in these experiments was prepared by a method suggested by Waran\*. When dilute ammonia is acted on by bromine water, the resulting nitrogen is free from all impurities except water-vapour.

The amount of this gas adsorbed was very small compared with that of carbon dioxide. The adsorption appeared to be instantaneous, and no time-effect could be detected; in one particular experiment the charcoal remained in contact with the gas for three days, and no diminution in pressure during that period of time could be detected.

The outgassing of the charcoal after nitrogen had been used was comparatively rapid; 6 hours' heating at  $450^{\circ}\text{C}.$  removed all the nitrogen that had been absorbed.

\* Phil. Mag. vol. xlii. p. 246 (1921).



The results obtained are given in Table III.

TABLE III.

Adsorption of Nitrogen at 15° C.

$p$ .	$q$ .	$\log_{10} \frac{\alpha}{P}$ .
$3.231 \times 10^{-3}$ mm.	0.1313	1.7050
5.727	0.2212	1.6829
10.88	0.3145	1.5570
13.40	0.3810	1.5498
15.69	0.5705	1.6567
20.76	0.7782	1.6698
25.69	0.9521	1.6645
30.57	1.120	1.6599
45.10	1.734	1.6808
63.56	2.742	1.7309
82.33	3.503	1.7249
99.64	5.066	1.8022
108.8	5.588	1.8066
117.0	6.642	1.8494

The relation between  $p$  and  $q$  is shown in fig. 2 (*b*). The curve is different from the others obtained, in that it is convex towards the  $p$  axis. At pressures below  $30 \times 10^{-3}$  mm. there is a linear relationship, and this part of the curve has been enlarged in fig. 3 (*b*). As in the case with the carbon dioxide adsorption isotherm, the curve is continuous from the lowest to the highest pressures.

The quantities  $\log_{10} \alpha$  and  $\log_{10} P$  are plotted in fig. 4 (*b*), and the resulting curve is similar to the adsorption isotherm of nitrogen in that it is convex towards the  $\log_{10} P$  axis. The curve below  $40 \times 10^{-3}$  is practically a straight line.

The values of  $\frac{1}{n}$  have been determined for various mean pressures, and are given in Table IV.

These values increase with rise in pressure, which result differs from that obtained by Claude and Titoff, and is also the reverse of that given by carbon dioxide.

The result of plotting  $\log_{10} \frac{\alpha}{P}$  and  $q$  is given in fig. 5 (*b*).

Below  $30 \times 10^{-3}$  mm. the curve is convex to the  $q$  axis, but above this pressure there is a linear relation between the

TABLE IV.

Values of  $\frac{1}{n}$  for Nitrogen in the equation  $\alpha = kP^{\frac{1}{n}}$ .

Mean Pressure.	4.479 $\times 10^{-3}$ mm.	10.72 $\times 10^{-3}$	23.13 $\times 10^{-3}$	42.52 $\times 10^{-3}$	63.80 $\times 10^{-3}$	82.22 $\times 10^{-3}$	104.1 $\times 10^{-3}$
$\frac{1}{n} \dots$	0.910	0.940	1.02	1.14	1.12	1.41	1.60

two quantities. It is, in fact, the reverse of that obtained with carbon dioxide. The values of  $A_0$  and  $A_1$  in the equation

$$\log_{10} \frac{c}{P} = A_0 - A_1 \alpha.$$

are

$$A_0 = 0.32; \quad A_1 = 27.4.$$

### c. Oxygen.

Oxygen was prepared by the action of acidulated potassium permanganate solution on hydrogen peroxide. These liquids were placed in Waran's \* apparatus and the gas stored over phosphorus pentoxide before use.

It is well known that oxygen attains equilibrium, when in contact with charcoal at high pressures, only after the lapse of long periods of time, and this was found to be the case at the very low pressures used in these experiments. Within the range  $10^{-5}$  to  $10^{-3}$  mm. the rate of absorption was rapid, and equilibrium was practically reached within 30 minutes. Above  $10^{-3}$  mm. the time required increased as the pressure was raised, and, at the highest pressures used, definite equilibrium was not attained after 5 days.

As stated previously, it was found impossible to remove all of the adsorbed oxygen by outgassing. This retentivity effect has been investigated by Lowry and Hulett †, who found that one-half of the adsorbed oxygen could be recovered at the ordinary outgassing temperature, but it was necessary to heat the charcoal to  $1000^\circ \text{C}$ . to recover the remaining gas, and this remainder was then emitted as carbon monoxide and carbon dioxide.

It was expected that as the boiling-point of carbon dioxide is higher than that of oxygen the amount of the latter gas

\* *Loc. cit.*

† Jour. Amer. Chem. Soc. vol. xlii. p. 1401 (1920).

adsorbed would be less than that of the carbon dioxide, but in actual practice the quantities adsorbed were much greater. This may have been due to one or two reasons or a combination of both; either the previous gassings and outgassings had improved the adsorptive capacity of the charcoal, or a chemical compound may have been formed. Lowry and Hulett suggest that the adsorption of oxygen is accompanied by the formation of a carbon-oxygen complex, a stable solid oxide of carbon, at the surface of the charcoal at ordinary temperatures, but decomposed by heating to  $1000^{\circ}\text{C}$ . it dissociates into carbon monoxide and carbon dioxide. This second reason also accounts for the inability to remove all the adsorbed gas at  $450^{\circ}\text{C}$ .

In the results shown in Table V. it was assumed that equilibrium had been attained, at the higher pressures, after five days had elapsed. The amount adsorbed after this period, though measurable, was small compared with the total amount that had disappeared previously. The temperature throughout the investigation was slightly higher than for carbon dioxide, the mean value being  $22^{\circ}\text{C}$ .

TABLE V.  
Adsorption of Oxygen at  $22^{\circ}\text{C}$ .

$p$	$q$ .	$\log_{10} \frac{q}{p}$ .
$0.136 \times 10^{-3} \text{ mm.}$	2.299	2.3240
0.200	4.647	2.4622
0.253	6.955	2.5352
0.298	9.204	2.5858
0.375	11.47	2.5816
0.464	15.88	2.6304
0.608	22.48	2.6638
0.770	28.95	2.6712
1.011	39.50	2.6879
1.271	49.87	2.6897
1.582	62.19	2.6891
1.830	76.35	2.7163
2.452	95.85	2.6880
5.921	203.2	2.6315
9.277	274.2	2.5667
18.04	385.3	2.4256
33.95	506.2	2.2696
60.19	624.5	2.1120
74.49	670.1	2.0501

The adsorption isotherm for oxygen shown in fig. 2 (c) is similar in all respects to that obtained with carbon dioxide. At pressures below  $2.5 \times 10^{-3}$  mm. a linear relation holds, but above this pressure the curve is concave to the pressure-axis. The lower range of readings is shown in fig. 3 (c), and, as with the carbon-dioxide isotherm, the curve does not pass through the origin, but meets the pressure-axis at  $8 \times 10^{-5}$  mm. It is assumed that below this pressure the quantity adsorbed cannot be measured by the present apparatus.

The relation between  $\log_{10} \alpha$  and  $\log_{10} P$ —fig. 3 (c)—resembles that for carbon dioxide, but at no pressure is a linear relationship evident. The values of  $\frac{1}{n}$  calculated from this curve are given in Table VI., and, as is to be expected from the shape of the curve,  $\frac{1}{n}$  decreases with increase in pressure. At the lower pressures this rate of decrease is rapid, but at higher pressures it becomes less, from which it is inferred that  $\frac{1}{n}$  approaches a constant value.

TABLE VI.

Values of  $\frac{1}{n}$  for Oxygen in the equation  $\alpha = kP^{\frac{1}{n}}$ .

Mean Pressure.	0.168 $\times 10^{-3}$ mm.	0.287 $\times 10^{-3}$ .	0.494 $\times 10^{-3}$ .	1.219 $\times 10^{-3}$ .	2.895 $\times 10^{-3}$ .	6.618 $\times 10^{-3}$ .	13.67 $\times 10^{-3}$ .	26.00 $\times 10^{-3}$ .	47.07 $\times 10^{-3}$ .
$\frac{1}{n}$	1.82	1.44	1.39	1.11	0.915	0.673	0.512	0.432	0.366

Plotting values of  $\log_{10} \frac{\alpha}{P}$  and  $q$ , the curve given in fig. 5 (c) is obtained. Concave to the  $q$  axis at low pressures it becomes a straight line at higher pressures. The values of the constants for this portion are  $A_0 = 2.88$ ;  $A_1 = 0.922$ .

The results for oxygen below  $2.5 \times 10^{-3}$  mm. are best represented by a linear relation between  $P$  and  $\alpha$ , but above  $4 \times 10^{-3}$  mm. the equation

$$\log_{10} \frac{\alpha}{P} = A_0 - A_1 \alpha$$

gives an approximately true relation between  $\alpha$  and  $P$ .

d. *Carbon Monoxide.*

Carbon monoxide was prepared by heating pure oxalic acid and concentrated sulphuric acid in a flask. The evolved gases were first passed through a wash-bottle and scrubbing chamber containing concentrated caustic potash solution, which removed carbon dioxide from the mixture. The resultant carbon monoxide then passed through phosphorus pentoxide and was stored in a bulb.

A new sample of charcoal was taken for this gas, as it was found that the old sample could not be effectively cleaned of the oxygen retained.

The amount of gas adsorbed was greater than with nitrogen, but less than with carbon dioxide. The adsorption was rapid and equilibrium was attained in 30 minutes; at the higher pressures no time-effect could be detected. Outgassing was complete at 450° C. at the end of 10 hours.

The results obtained with this gas are shown in Table VII.

TABLE VII.

Adsorption of Carbon Monoxide at 20° C.

$p$ .	$q$ .	$\log_{10} \frac{q}{p}$ .
$4.267 \times 10^{-3}$ mm.	1.181	0.5308
9.279	1.874	0.3936
14.42	2.417	0.3129
19.21	3.152	0.3036
24.27	3.730	0.2752
29.23	4.445	0.2706
34.66	4.986	0.2464
44.26	6.463	0.2529
55.08	7.551	0.2255
69.88	8.694	0.1833
85.56	10.31	0.1798

The adsorption isotherm is shown in fig. 2 (*d*), and is intermediate in shape to those for nitrogen and carbon dioxide. It is straight up to  $40 \times 10^{-3}$  mm., becoming slightly concave to the  $p$  axis above this pressure. That part of the curve below  $30 \times 10^{-3}$  mm. is shown on a larger scale in fig. 3 (*d*).

The result obtained by plotting  $\log_{10} \alpha$  and  $\log_{10} P$ —fig. 4 (*d*)—is similar to the corresponding curve for nitrogen; the concavity is towards the  $\log_{10} \alpha$  axis, but becomes zero

above  $12 \times 10^{-3}$  mm. The value of  $\frac{1}{n}$  for the latter part, *i.e.* from  $12 \times 10^{-3}$  mm. to  $85 \times 10^{-3}$  mm., is 0.826; below  $12 \times 10^{-3}$  mm. the mean value of  $\frac{1}{n}$  is 0.600 at a mean pressure of  $6.6 \times 10^{-3}$  mm.

The  $\log_{10} \frac{\alpha}{P}$ ,  $q$  curve—fig. 5 (*d*)—resembles the corresponding nitrogen curve, but the slope of the straight portion is in the same direction as that of the curves for oxygen and carbon dioxide. The values of the constants for this portion are  $A_0 = 0.316$  :  $A_1 = 6.666$ .

#### 4. DISCUSSION.

In considering the curves obtained for the various gases, it is advantageous to place the gases in the order of increasing boiling-points, *i.e.* nitrogen, carbon monoxide, oxygen, and carbon dioxide. The order of changes in the shape of the adsorption isotherm follows the same sequence. The nitrogen isotherm is a straight line for a considerable portion of its length, and then becomes slightly convex to the pressure-axis; the carbon-monoxide isotherm is straight for about the same range of pressure as nitrogen, and then slightly concave to the pressure-axis; the oxygen isotherm is straight for the same range of pressure and then decidedly concave to the pressure-axis; the carbon-dioxide isotherm is straight for only a small range of pressure, and its concavity to the pressure-axis above this range is of the same order as that of the oxygen isotherm.

The change in shape in the  $\log_{10} P$ ,  $\log_{10} \alpha$  curves is also in the same sequence. That for nitrogen is slightly convex to the  $\log_{10} P$  axis for the whole range covered; the carbon-monoxide curve is slightly convex for a short portion, becoming a straight line for the higher pressures; the oxygen curve is concave to this axis for the whole range; the carbon-dioxide curve is concave for a short portion, after which it is straight.

A similar change is noted in the  $\log_{10} \frac{\alpha}{P}$ ,  $q$  curves, the nitrogen curve being convex to the  $q$  axis for a small range, and then changing into a straight line sloping away from the  $q$  axis; the carbon-monoxide curve is also convex for the same range as nitrogen, becoming a straight line with a

slope towards the  $q$  axis; the oxygen and carbon-dioxide curves are both concave to the  $q$  axis, becoming straight lines whose slopes to the  $q$  axis are greater than the corresponding slope of the carbon-monoxide curve.

The order of the quantities of gas adsorbed, neglecting the anomalous case of oxygen, is also in the same sequence.

At pressures below a critical pressure which varies for the various gases, the adsorption isotherm is best represented by the type of equation

$$\alpha = kP;$$

$$\text{i. e.} \quad \frac{1}{n} = 1.$$

This critical pressure is comparatively high for the gases of low boiling-point, being about  $35 \times 10^{-3}$  mm. for carbon monoxide and nitrogen; but with those gases of higher boiling-point and which are more easily adsorbed the critical pressure is considerably lower, being  $2.5 \times 10^{-3}$  mm. for oxygen and  $1.5 \times 10^{-3}$  for carbon dioxide. Hence it appears that the higher the boiling-point of the gas the lower is the critical pressure below which it can be assumed that the adsorption isotherm is a straight line.

The fact that  $\frac{1}{n}$  does not equal unity at pressures below the critical pressure mentioned above suggests that

$$\alpha = kP^{\frac{1}{n}}$$

is not valid throughout a large pressure-range, although any curve of this type will be approximately a straight line for small values of  $\alpha$  and  $P$ , *i. e.* near the origin; but from theoretical considerations it can be shown that the slope of this curve does not even approximate to the slopes obtained experimentally.

Transforming this equation to the form

$$P = \left(\frac{\alpha}{k}\right)^n,$$

we have

$$\frac{dP}{d\alpha} = \frac{n\alpha^{n-1}}{k^n}.$$

Therefore at  $\alpha = 0$ ,  $\frac{dP}{d\alpha} = 0$  and the curve is tangential

to the  $\alpha$  axis at the origin. So that

$$\alpha = kP^{\frac{1}{n}}$$

cannot be accepted as representing the relation between  $\alpha$  and  $P$  at the pressures used in these experiments.

A consideration of the second type of adsorption equation suggested gives entirely different results :

$$\log_{10} \frac{\alpha}{P} = A_0 - A_1 \alpha.$$

Then

$$\frac{\alpha}{P} = e^{2.303 (A_0 - A_1 \alpha)},$$

$$\frac{dP}{d\alpha} = e^{-2.303 (A_0 - A_1 \alpha)} + 2.303 A_1 \alpha e^{-2.303 (A_0 - A_1 \alpha)}.$$

At  $\alpha=0$ ,

$$\frac{dP}{d\alpha} = e^{-2.303 A_0},$$

and the curve has therefore a definite slope at the origin.

Considering the values of  $\frac{dP}{d\alpha}$  obtained by calculation from the above equation and also from the graphs in fig. 3, we have:

for Nitrogen  $\frac{dP}{d\alpha} = 4.055,$

the experimental value is 2.433 ;

for Carbon Monoxide  $\frac{dP}{d\alpha} = 0.479,$

the experimental value is 0.618 ;

for Oxygen  $\frac{dP}{d\alpha} = 0.00132,$

the experimental value is 0.00437 ;

for Carbon Dioxide  $\frac{dP}{d\alpha} = 0.00163,$

and the experimental value is 0.00335.

Although the calculated and experimental values of  $\frac{dP}{d\alpha}$



do not agree absolutely, yet a comparison of their orders of magnitude suggests that

$$\log_{10} \frac{\alpha}{P} = A_0 - A_1 \alpha$$

represents more accurately the adsorption isotherm than the usually recognized form

$$\alpha = kP^{\frac{1}{n}}.$$

The variation in the calculated and experimental results is due probably to the fact that it was necessary to calculate the values of  $A_0$  from the more advanced portions of the curve.

At very low pressures, and correspondingly low values of  $\alpha$ , the term  $A_1 \alpha$  is very small compared with the value of  $A_0$ , and at this stage

$$\log_{10} \frac{\alpha}{P} = A_0 = \text{constant};$$

i. e. there is a linear relation between  $\alpha$  and  $P$  at very low pressures. This fact has been noted previously.

That  $\log_{10} \frac{\alpha}{P}$  is a constant for a short range is illustrated in the curves for carbon dioxide and oxygen shown in fig. 5; with these gases the pressure-range over which this condition holds is from  $0.5 \times 10^{-3}$  to  $1.75 \times 10^{-3}$  mm. for carbon dioxide, and from  $0.5 \times 10^{-3}$  to  $4.0 \times 10^{-3}$  mm. for oxygen. The value of  $A_0$  as given by the horizontal portion of the graph is slightly less than that obtained by calculation from the straight portion, being 2.43 for carbon dioxide and 2.72 for oxygen. Similar results do not occur on the curves for nitrogen and carbon monoxide. This is due probably to the fact that measurements of adsorption were not made below  $4 \times 10^{-3}$  mm. for these gases.

At pressures below  $0.5 \times 10^{-3}$  mm. the results obtained do not agree with the formula. The sudden decrease in the value of  $\log_{10} \frac{\alpha}{P}$  must be accompanied by a change in the value of  $A_0$ , and to account for this change is very difficult. If the original assumptions from which Henry \* deduced

\* Phil. Mag. vol. xlv. p. ('89 (1922)).

the formula are examined, it is found that among other constants  $A_0$  includes an expression for the field of molecular force, and the internal heat of evaporation of the molecules from the surface.  $A_0$  is inversely proportional to the field of molecular force, and the heat of evaporation  $\lambda$  affects a

term  $\frac{\lambda}{\epsilon RT}$ , where  $\epsilon$ ,  $R$ ,  $T$  have their usual significance. Therefore for  $A_0$  to decrease, it must be assumed that there is either a sudden change in the field of molecular force which causes it to increase with decreasing pressure, or that the internal heat of evaporation decreases. Further investigation seems desirable.

### 5. SUMMARY.

1. A method for determining the quantities adsorbed by activated charcoal at very low pressures is described.

2. Results have been obtained for nitrogen, carbon monoxide, oxygen, and carbon dioxide at air temperatures.

3. From a consideration of the adsorption isotherm of these gases, it is shown that the adsorption isotherm is better represented by

$$\log_{10} \frac{\alpha}{P} = A_0 - A_1 \alpha$$

than by the more usual equation

$$\alpha = kP^{\frac{1}{n}}.$$

4. At very low pressures the value of  $A_1 \alpha$  is negligible compared with that of  $A_0$ , and the relationship between  $\alpha$  and  $P$  is linear. The pressure at which this relationship no longer holds varies with the boiling-point of the gas; it decreases as the boiling-point increases.

In conclusion, the Author wishes to express his sincere thanks to Prof. F. H. Newman for suggesting this branch of research, and for the keen interest he has taken and the helpful suggestions made throughout.

IX. *Fraunhofer Diffraction Phenomena for a General Polygonal Aperture.* By ENOS E. WITMER, Ph.D., *Harrison Research Fellow, University of Pennsylvania* \*.

[Plate III.]

**A**LTHOUGH the Fraunhofer diffraction patterns for apertures of various simple geometrical shapes have been studied in the classical researches on diffraction, it does not seem to be generally known that the principal features of the pattern can in all cases be described in very simple terms. The principal pattern is a radiate pattern, the centre of which is the image of the luminous point. Corresponding to each side of the aperture there are two rays,  $180^\circ$  apart, each perpendicular to the side in question. On the patterns obtained with small apertures these rays do not stand out so prominently, which is undoubtedly the reason why they are not emphasized in the theory of diffraction, but as the size of the aperture increases the minor features of the pattern fade into insignificance, leaving only the radiate figure. These rays appear, for example, on night photographs taken with cameras having an iris diaphragm which produces a polygonal aperture; each light source of sufficiently small angular diameter appears on such a picture as the centre of a number of divergent rays.

Historically it may be of interest to note that Sir John Herschel† observed these ray patterns in his telescope. Lloyd‡ and J. W. Gordon§ also refer to them, while Airy|| worked out the mathematical theory for the case of the equilateral triangle, and showed that the principal pattern consists of six rays. Schwerd¶ derived mathematically the patterns for various simple geometrical apertures.

No one, however, seems to have demonstrated mathematically that, in the case of the general polygonal aperture, the principal pattern conforms to the description given above. This demonstration is made below. The theory shows, furthermore, that in certain cases these rays have a fringe structure, while in other cases they do not. This result seems to be new, and has subsequently been confirmed experimentally.

\* Communicated by Prof. C. B. Bazzoni.

† Sir John Herschel, 'Encyclopedia Metropolitana,' "Light," Art. 772.

‡ Lloyd, 'The Wave Theory of Light,' pp. 126-127.

§ J. W. Gordon, Proc. Phys. Soc. Lond. xxiv. pp. 422-448 (1912).

|| Airy, 'Mathematical Tracts,' pp. 316-318.

¶ Schwerd, *Die Beugungserscheinungen*.

The aperture is assumed to be plane. Using rectangular Cartesian coordinates, we shall take the plane of the aperture as the  $xy$ -plane, and the origin in or very near the aperture. Let  $(u_1, v_1, w_1)$  be the coordinates of the centre of the luminous disturbance incident on the aperture, and  $(u_0, v_0, w_0)$  the point in or very near the focal plane at which the effect is to be determined.

$$\begin{aligned}\text{Let} \quad \rho_1^2 &= u_1^2 + v_1^2 + w_1^2, \\ \rho_0^2 &= u_0^2 + v_0^2 + w_0^2.\end{aligned}$$

Then the effect at the point  $(u_0, v_0, w_0)$  is given in terms of the wave-function by the well-known formula \*

$$\phi_0(\tau) = -\frac{A}{\lambda} \frac{1}{\rho_1 \rho_0} \frac{\partial \rho_0}{\partial z} e^{ik\omega\tau} \iint i e^{i(px+gy)} dx dy, \quad (1)$$

where the integration is over the surface of the aperture, and

$$\left. \begin{aligned} p &= \frac{2\pi}{\lambda} \frac{1}{\rho_0} (u_0 - u_1) \equiv \frac{2\pi}{\lambda} \frac{r}{\rho_0}, \\ q &= \frac{2\pi}{\lambda} \frac{1}{\rho_0} (v_0 - v_1) \equiv \frac{2\pi}{\lambda} \frac{s}{\rho_0}. \end{aligned} \right\} \quad \cdot \cdot \quad (2)$$

$A$  and  $\omega$  are constants,  $k = \frac{2\pi}{\lambda}$ ,  $\lambda$  is the wave-length of light,  $\tau$  is time, and  $i = \sqrt{-1}$ .

$$\text{Let} \quad \left. \begin{aligned} r &= u_0 - u_1, \\ s &= v_0 - v_1, \\ t &= w_0 - w_1. \end{aligned} \right\} \cdot \cdot \cdot \cdot \quad (3)$$

Since in the case of Fraunhofer diffraction phenomena the centre  $(u_1, v_1, w_1)$  of the luminous disturbance incident on the aperture is the image of the radiant point,  $r, s$ , and  $t$  are the coordinates of the point considered on the screen of observation referred to the radiant point as origin. Hereafter, in referring to the point  $(u_0, v_0, w_0)$ , we shall use the coordinates  $(r, s, t)$ .

It is evident that we may rotate the  $x$ - and  $y$ -axes about the  $z$ -axis into any position we choose. We shall therefore choose these axes so as to make  $s=q=0$  for the particular point considered, thereby simplifying the integration in (1).

Now consider an aperture which has the shape of an

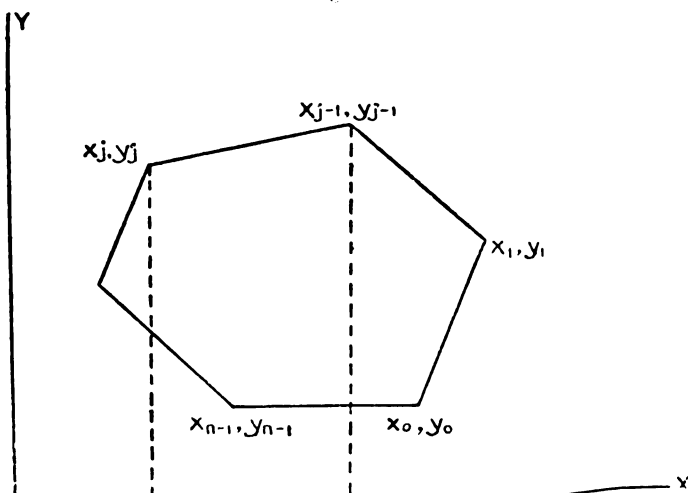
\* See Walker, 'Analytical Theory of Light' (Camb. Univ. Press, pp. 96-99).

irregular polygon of  $n$  sides. Let the  $xy$ -coordinates of the  $n$  vertices be

$$(x_0, y_0), (x_1, y_1), \dots, (x_{n-1}, y_{n-1}), (x_n, y_n) \equiv (x_0, y_0),$$

as indicated in fig. 1.

Fig. 1.



Let us call the side whose end-points are  $(x_{j-1}, y_{j-1})$  and  $(x_j, y_j)$  the side  $j$ , and the quadrilateral whose vertices are

$$(x_{j-1}, y_{j-1}), (x_j, y_j), (x_j, 0), (x_{j-1}, 0),$$

as is indicated in fig. 1, the quadrilateral  $j$ .

The equation of side  $j$  is

$$\frac{y_{j-1} - y}{x_{j-1} - x} = \frac{y_j - y}{x_j - x} = \frac{y_j - y_{j-1}}{x_j - x_{j-1}} = m, \quad \dots \quad (4)$$

whence

$$y_j - m_j x_j = y_{j-1} - m_j x_{j-1}. \quad \dots \quad (4a)$$

Since  $q=0$ , the integral in (1) taken over the quadrilateral  $j$  is

$$\iint e^{ipx} dx dy = \int_{x_j}^{x_{j-1}} i(y_j + m_j x - m_j x_j) e^{ipx} dx.$$

Using equation (4a) we obtain

$$\iint e^{ipx} dx dy = \frac{1}{p} (y_{j-1} e^{ipx_{j-1}} - y_j e^{ipx_j}) + \frac{im_j}{p^2} (e^{ipx_{j-1}} - e^{ipx_j}). \quad (5)$$

The integral over the polygon is evidently given by the expression

$$J(r, 0, t) \equiv \iint e^{ipx} dx dy = \sum_{j=1}^n \int_{x_j}^{x_{j-1}} i(y_j + m_j x - m_j x_j) e^{ipx} dx \\ = \sum_{j=1}^n \frac{im_j}{p^2} (e^{ipx_{j-1}} - e^{ipx_j}). \quad (6)$$

This is the expression for the integral  $J$  if none of the  $m_j$ 's are infinite. If the  $xy$ -axes have been so chosen as to make some of the slopes  $m_j$  infinite, we must evaluate the indeterminate terms in (6). Remembering that if  $m_\sigma = \infty$ ,  $x_\sigma = x_{\sigma-1}$ , we get in this case

$$0, t) = \sum_j \frac{im_j}{p^2} (e^{ipx_{j-1}} - e^{ipx_j}) + \sum_\sigma \frac{y_\sigma - y_{\sigma-1}}{p} e^{ipx_\sigma}, \quad (7)$$

where the first summation is over the finite slopes  $m_j$  and the second over the infinite slopes. Since  $x_\sigma = x_{\sigma-1}$ ,  $y_\sigma - y_{\sigma-1} = \pm l_\sigma$ , where  $l_\sigma$  is the length of the side  $\sigma$ .

The terms in  $\frac{1}{p^2}$  in (6) and (7) will be negligible in comparison with those in  $\frac{1}{p}$ , provided that in general

$$\frac{m_j}{p(y_\sigma - y_{\sigma-1})} \text{ is small.}$$

This will be so, if  $pL$  is sufficiently large, where  $L$  is the average length of a side of the polygonal aperture. Using equation (2), this condition reduces to the condition that  $\frac{1}{\lambda} \frac{L}{\rho_0} r$  be sufficiently large. Since the point under consideration is  $(r, 0, t)$  for the particular plane of observation  $t=0$ , which is parallel to the plane of the aperture,  $r$  is the radial distance of the point considered from the image of the luminous point. Since  $\lambda$  is always very small in the case of visible or ultra-violet light, this is not a stringent condition, but it does exclude a certain region about the image of the luminous point where  $r$  is too small. Under this condition (6) and (7) reduce respectively to

$$J(r, 0, t) = 0 \quad (8)$$

and 
$$J(r, 0, t) = \sum_\sigma \frac{y_\sigma - y_{\sigma-1}}{p} e^{ipx_\sigma}. \quad (9)$$

Let us consider the expression  $J$  in equation (9). Using equation (2), we see that  $J(r, 0, t) = J(r)$ —that is,  $J$  is

a function of  $r$  alone, all the other quantities being constants. It can be shown that  $J(r)$  cannot be identically zero in any case, since no two of the  $x_\sigma$ 's can be equal. Furthermore,  $J(r)$  can vanish for only an enumerable infinity of values of  $r$ , so that the values of  $r$  at which  $J(r) \neq 0$ , regarded as a set of points, is *everywhere dense*. Since in any practical case the range of  $r$  is limited, it is easy to see that  $J(r)$  will vanish for only a finite number of values of  $r$  in that range.

The intensity  $I$  is obtained by substituting  $J(r, 0, t)$  for the integral in (1), and multiplying this result by its conjugate. Since  $I(r, 0, t)$  vanishes when, and only when,  $J(r, 0, t)$  vanishes, we see from (8) and (9) that  $I=0$  at all the points  $(r, 0, t)$  except when some of the slopes are infinite, in which case the intensity is finite at an everywhere dense set of points in the  $rt$ -plane in a certain region about the image of the luminous point. Now the fact that the slope of a side is infinite means that the  $y$ -axis is parallel to that side, and the  $rt$ -plane is perpendicular to the  $y$ -axis. Regarding the  $xy$ -axes as rotating about the  $z$ -axis, and therefore the  $rs$ -axes as rotating about the  $t$ -axis, it follows that all the points of finite intensity lie in planes through the image of the radiant point that are perpendicular to the sides of the aperture, and on these planes the points of finite intensity are everywhere dense in a certain region about the image of the luminous point. It is easily seen now that the pattern on any plane through the image of the radiant point is a radiate pattern whose centre is the image point, and that corresponding to each side of the aperture there are two bright rays,  $180^\circ$  apart, perpendicular to the side in question. We have therefore demonstrated the rule stated in the first paragraph.

Having demonstrated the existence of these rays, we shall next consider their structure. We shall limit our discussion to the pattern on the plane  $t=0$ , which is parallel to the plane of the aperture. In this case  $r$  is the radial distance of the point considered  $(r, 0, 0)$  from the image of the radiant point. Since  $t$  does not appear in the formulas for  $I$  and  $J$ , the pattern on any other plane  $P$  through the image of the radiant point is obtained by projecting the pattern on the plane  $t=0$  on to the plane  $P$  by a family of lines normal to the plane of aperture.

First consider the case when there is no other side parallel to the side in question, which we will assume to be the side 1. Then from (9) the corresponding value of  $J$  is

$$J(r, 0, t) = \frac{y_1 - y_0}{p} e^{ipr_1}, \quad . \quad . \quad . \quad (10)$$

and the intensity of the corresponding ray is

$$I(r, 0, t) = \left( \frac{A}{2\pi} \frac{1}{\rho_1} \frac{\partial \rho_0}{\partial z} \right)^2 \frac{l_1^2}{r^2} \dots \quad (11)$$

Equation (11) shows that in this case the rays do not have a fringe structure; but that the intensity falls off uniformly as the inverse square of the radial distance. Furthermore, the intensity is proportional to the square of the length of the corresponding side.

When two sides of the aperture, 1 and  $\sigma$ , are parallel, the corresponding value of  $J$  is

$$\begin{aligned} J(r, 0, t) &= \frac{1}{p} [(y_1 - y_0)e^{ipx_1} + (y_\sigma - y_{\sigma-1})e^{ipx_\sigma}] \\ &= \frac{e^{ip(x_1 + x_\sigma)}}{p} [(l_1 - l_\sigma) \cos ap + i(l_1 + l_\sigma) \sin ap], \quad (12) \end{aligned}$$

where  $2a = x_1 - x_\sigma =$  the distance between the parallel sides. Hence the intensity distribution\* along the corresponding rays is

$$\begin{aligned} I(r, 0, t) &= \left[ \frac{A}{2\pi} \frac{1}{\rho_1} \frac{\partial \rho_0}{\partial z} \frac{1}{r} \right]^2 [(l_1 - l_\sigma)^2 \cos^2 ap \\ &\quad + (l_1 + l_\sigma)^2 \sin^2 ap]. \quad (13) \end{aligned}$$

In this case the corresponding rays exhibit maxima and minima of intensity which are more or less pronounced according as  $l_1$  and  $l_\sigma$  are or are not equal.

These two cases are the ones most commonly met with. It is only in the case of polygons with re-entrant angles that more than two sides can be parallel to each other, and the formulas for the intensity of the corresponding rays become complicated.

These conclusions as to the structure of the rays were verified experimentally. Photographs were taken with a large camera equipped with a telephoto lens. A carbon arc with a cap attachment for getting a point source was used as the source of light. The diffracting diaphragm, which was made of razor-blades fastened on cardboard, was set up in front of the lens. Fig. 2 (Pl. III.) shows the pattern obtained with a triangular aperture, the triangle being approximately equilateral. These rays do not show a fringe structure. This same diaphragm was taken and the triangle converted into a trapezoid by adding another blade in such a way as to cut off about half the altitude. The pattern

\* Equation (13) applies to the case when  $(y_1 - y_0)$  and  $(y_\sigma - y_{\sigma-1})$  have opposite signs. If these two quantities have like signs, which can occur only in the case of a polygon with re-entrant angles, the quantities  $(l_1 - l_\sigma)$  and  $(l_1 + l_\sigma)$  must be interchanged in equation (13).



obtained with this diaphragm is shown in fig. 3 (Pl. III.). The vertical rays, which are due to the parallel sides of the aperture, have a fringe structure in accordance with theory. The other four rays are due to the remaining sides of the trapezoid, and show no fringes. The differences in the intensities of the vertical and non-vertical rays is due to the differences in the length of the sides producing the rays, as equations (11) and (13) show. The fringes in fig. 3 (Pl. III.) show much more distinctly on the original negative than in the reproduction, and the central part of the patterns in both figures is obscured by halation.

A number of figures, not published here, were also obtained with large diffracting apertures of various shapes, using an ordinary camera and a point source of light. In some cases the iris diaphragm of the camera, set at F 8 or F 11, was used as the diffracting aperture. In every case the patterns conform to the description given above, except that with the large apertures the fringe structure does not appear because the fringes are too fine-grained.

#### *Summary.*

The preceding analysis demonstrates, and experiment verifies, the following conclusions:—

(1) The most prominent features of the Fraunhofer diffraction pattern for a general polygonal aperture form a radiate figure, consisting of bright rays diverging from the image of the luminous point. Corresponding to each side of the aperture there are two rays,  $180^\circ$  apart, perpendicular to that side.

(2) These rays may, or may not, have a fringe structure. If there is no other side of the aperture parallel to the side in question, the two rays corresponding do not have a fringe structure, the intensity in each ray decreasing uniformly from the centre outward. If, however, one or more sides of the aperture are parallel to the side in question, the two rays corresponding exhibit maxima and minima of intensity.

These conclusions are based on an approximation which is not valid in a certain region about the centre of the figure, a region which is in many cases vanishingly small, but in other cases is very large.

In conclusion, the writer wishes to acknowledge his indebtedness to Dr. H. C. Richards for valuable suggestions regarding the experimental work.

Research Section,  
Randal Morgan Laboratory of Physics,  
University of Pennsylvania,  
July 27, 1925.

X. *Langevin's Theory of Ionic Mobility.* By H. R. HASSÉ, M.A., D.Sc., *Professor of Mathematics in the University of Bristol* \*.

THE calculations given in this paper originated in the proposal to apply to the theory of ionic mobility the rigorous methods which have been introduced into the kinetic theory of gases by Chapman† and Enskog‡. It is known from the work of these investigators that calculations based on the use of the "mean free path," whilst they give a general descriptive view of the phenomena, may lead to quite erroneous results, not only in regard to the numerical factors occurring in the equations, but also in regard to the dependence of the phenomena on the various physical quantities involved. The results obtained by Chapman and Enskog have cleared up many points of difficulty which had arisen, and brought about a harmony and a consistency which was lacking in the older treatments.

The need of a satisfactory theory of mobility was pointed out to me by my colleague Professor Tyndall, and I had completed some of the necessary calculations before discovering that the subject had been exhaustively treated by Langevin§ in a paper which is of fundamental importance, and which seems to have been frequently neglected, and sometimes misunderstood, by writers on this subject.

Apart from its application to mobility Langevin's work is of great interest, as it provides the only case, up to the present time, in which a detailed treatment of the influence on elastic collisions of attractive forces of any magnitude has been given. Sutherland's well-known procedure, which has been treated rigorously by Enskog and James||, only deals with the effect of weak forces of attraction, and is therefore only a first approximation to the general case. For this reason, and also in view of future applications, it was considered worth while to make a recalculation of the numerical part of the paper, the results of which are given by Langevin in a curve from which they cannot be obtained with any great accuracy.

\* Communicated by the Author.

† Chapman, *Phil. Trans.* A, cexi. (1912), ccxvi. (1916), and ccxvii. (1918).

‡ Enskog, 'Kinetische Theorie der Vorgänge in mässig verdünnten Gasen' (1917).

§ Langevin, *Ann. de Chimie et de Physique*, (8) v. p. 245 (1905).

|| Enskog, *loc. cit.*; James, *Proc. Cam. Phil. Soc.* xx. p. 447 (1921).

## I. GENERAL STATEMENT OF THE THEORY.

1. *Langevin's Theory.*

The problem of the motion of the ions under the influence of an external field and the field of the molecules is a problem in the kinetic theory of diffusion. The ion is represented as a positive or negative charge of magnitude  $e$ , the charge on an electron, and the model chosen for the molecule is that of a perfectly conducting sphere. The attractive force between the ion and the molecule is then due to the induced charge on the latter, and is equal to

$$\frac{e^2 a^3 (2r^2 - a^2)}{r^3 (r^2 - a^2)^2}, \quad \dots \dots \dots (1)$$

where  $a$  is the electrical radius of the molecule, and  $r$  the distance of the ion from the centre of the sphere\*.

If  $r$  is assumed to be always large compared with  $a$ , this force is

$$2e^2 a^3 / r^5, \quad \dots \dots \dots (2)$$

and if  $K$  is the dielectric constant of the gas containing  $N$  molecules per unit volume, we have

$$K - 1 = 4\pi N a^3 \dagger. \quad \dots \dots \dots (3)$$

whence the force of attraction is given by

$$(K - 1) e^2 / 2\pi N r^5. \quad \dots \dots \dots (4)$$

The expression (4) for the attractive force is also the first term in a series which would give the force on any assumption as to the size and shape of the neutral molecules.

The rigorous mathematical treatment of problems in the kinetic theory is very complicated, and the results can only be obtained by a process of successive approximation. Fortunately, the first approximation is a very good one and, in the case of diffusion under consideration, this was obtained by Langevin in the paper referred to: (i.) when the molecules are perfectly elastic spheres, and (ii.) when in addition the molecules exert attractive forces of the type given by equation (4).

\* Cf. J. J. Thomson, 'Elements of the Mathematical Theory of Electricity and Magnetism,' 5th edition, p. 114.

† Cf. Jeans, 'Mathematical Theory of Electricity and Magnetism,' p. 131 (1908).

Using, to a large extent, Langevin's notation, the mobility  $k$  is expressed in the form

$$k = \frac{A}{\sqrt{\rho}(K-1)} \left(1 + \frac{m}{M}\right)^{\frac{1}{2}}, \dots (5)$$

where  $\rho$  is the density of the gas,  $M$  the mass of the ion, and  $m$  that of a molecule of the gas, whose concentration is large compared with that of the ions, and  $A$  is a numerical coefficient. The value of  $A$  has been calculated in the case of a repulsive centre of force varying inversely as the  $n$ th power of the distance for various values of  $n$  by Maxwell ( $n=5$ ), and Chapman ( $n=7, 9, 11, 15$ , and  $\infty$ ) \*.

When the force is attractive, and collisions take place, the value of  $A$  will depend on the comparative effect of the attractive forces and the elastic collisions. Langevin introduces a symbol  $\mu$  ( $\equiv \lambda^{-1}$ ) given by

$$\mu^2 = \frac{(K-1)e^2}{8\pi p \sigma^4}, \quad \lambda^2 = \frac{8\pi p \sigma^4}{(K-1)e^2}, \dots (6)$$

where  $p$  is the pressure of the gas, and  $\sigma$  is the distance between the centres of the molecule and the ion at the instant of collision, and  $A$  is then calculated as a function of  $\lambda$ ; it is this calculation of  $A$  in terms of  $\lambda$  which is an important feature of Langevin's paper.

When  $\lambda$  is small, either  $\sigma$  must be small or  $(K-1)$  large, so that the attractive forces are of much greater importance than the collisions, and in this case  $A$  tends to a limiting value given by Langevin as 0.505.

Equation (5) may be written in the form

$$k = \lambda A \frac{e}{\sigma^2(8\pi p \rho)^{\frac{1}{2}}} \left(1 + \frac{m}{M}\right)^{\frac{1}{2}}, \dots (7)$$

and in the case when  $\lambda$  is large, i. e. the attracting forces are weak,  $\lambda A \rightarrow 0.75$ , so that  $k$  tends to the value

$$\frac{3}{4} \frac{e}{\sigma^2(8\pi p \rho)^{\frac{1}{2}}} \left(1 + \frac{m}{M}\right)^{\frac{1}{2}} \dots (8)$$

Experiments on positive ions show that the mobility varies inversely as the pressure over a large range of pressure. For negative ions this law does not hold over as wide a range, which may be attributed to the presence at low pressures of free electrons in this case. If the temperature is kept constant,  $\rho$  will vary as  $p$ , and if we may assume that

\* Chapman, Mem. and Proc. Man. Lit. and Phil. Soc. lxvi. p. 1 (1922).

( $K-1$ ) varies also as  $p$  in accordance with the Clausius-Mosotti theory of dielectrics, then from (6)  $\lambda$  is independent of the pressure, and therefore from (5) and (7) the mobility should vary as  $p^{-1}$ . Thus these formulæ are in agreement with those given by other theories in predicting the same law of variation of mobility with pressure.

Before proceeding further, it is necessary to inquire how allowance can be made for the fact that equation (5) is only a first approximation to the correct formula. It has been shown by Chapman and Enskog that, in the case of elastic collisions, the equation for the diffusion of gases, and hence equation (5) which is derived from it, gives results which are about 13 per cent. too small, and that the equation is exact in the other extreme case, when we are dealing only with forces varying inversely as the fifth power of the distance. For intermediate cases where both collisions and attractive forces are operative, we may safely say that the correcting factor will lie between 1.00 and 1.13, but its value has not yet been determined, and it will be evident later on that its calculation would introduce a refinement which is not justified by the present state of either the theoretical or the experimental side of the subject. In the calculations of mobility in Section III. it has therefore been considered sufficient to take the value of the Chapman-Enskog correcting factor as unity, except when  $\lambda \geq 2.3$  (when the effect of the collisions predominates), in which case its value has been taken as 1.13.

## 2. *Comparison with other Theories.*

The important features of Langevin's theory can best be brought out by a discussion of certain other formulæ for the mobility which have been given, and which are based on the older type of kinetic theory.

Wellisch\* gave an expression for  $k$  which, in the notation of this paper, is

$$k = \frac{e}{\pi\sigma^2} (3p\rho)^{-\frac{1}{2}} \left(\frac{m}{M}\right)^{\frac{1}{2}} \left(1 + \frac{M}{m}\right)^{-\frac{1}{2}} \left(1 + \frac{2}{3\lambda^2}\right)^{-1}, \quad (9)$$

which cannot be expected to apply to strong attractive forces since  $k \rightarrow 0$  as  $\lambda \rightarrow 0$ . For weak attractive forces when  $\lambda$  is large, (9) becomes

$$k = \frac{e}{\pi\sigma^2} (3p\rho)^{-\frac{1}{2}} \left(\frac{m}{M}\right)^{\frac{1}{2}} \left(1 + \frac{M}{m}\right)^{-\frac{1}{2}}. \quad (10)$$

\* Wellisch, Phil. Trans. A, ccix. p. 249 (1909).

Another example of a formula for the mobility of which use has been made in the discussion of experimental results is that given by J. J. Thomson\* in the course of an interesting consideration of theories of ionic mobility, viz. :—

$$k = \frac{3}{4} \frac{e}{\pi \sigma^2} (3p\rho)^{-\frac{1}{2}} \frac{\left(1 + \frac{m}{3M}\right)}{\left(1 + \frac{m}{5M}\right)} \left(1 + \frac{m}{M}\right)^{\frac{1}{2}}, \quad (11)$$

where  $m \leq M$ , the only case we need consider.

This formula is based on the "mean free path" method, corrected for the phenomenon of persistence of velocity, and assumes that the only interaction of a molecule and an ion is that of an elastic collision.

Equations (8), (10), and (11), which all apply to weak attractive forces, are directly comparable, and it is evident that they differ both in their numerical values and in their dependence on the ratio of  $m$  to  $M$ .

For the case of a mono-molecular ion when  $M=m$ , the formulæ will give values for the mobility in the ratio

$$1 : \frac{4}{3} \left(\frac{2}{3\pi}\right)^{\frac{1}{2}} : \frac{20}{9} \left(\frac{2}{3\pi}\right)^{\frac{1}{2}},$$

or

$$1 : 0.614 : 1.023.$$

This will account to a great extent for the fact that Wellisch's calculated values for such an ion are much smaller than those given in Section III. as determined from Langevin's formula.

As regards the dependence on the ratio  $m/M$ , we see that as this ratio increases from 0 to 1, the mobility, as calculated from the formulæ (8), (10), and (11), will increase in the ratios

$$1 \text{ to } \sqrt{2}, \quad 0 \text{ to } 1/\sqrt{2}, \quad \text{and} \quad 1 \text{ to } 10\sqrt{2}/9,$$

respectively. Now it is known from experiment that the mobility of an ion depends only on the gas into which it is introduced. The simplest way of accounting for this important fact is to make the formulæ almost independent of the mass  $M$  of the ion, which in the case of (8) and (11) can be done by taking  $M$  to be large compared with  $m$ , i. e. by assuming that the ion is clustered with molecules of the gas. This is not possible on Wellisch's formula (10), which will give mobilities varying widely with changes in the value of the ratio  $m/M$ .

\* J. J. Thomson, *Proc. Phys. Soc.* xxvii. p. 94 (1914-15).

J. J. Thomson has, in addition to the case of elastic collisions, considered also the other extreme case of strong attractive forces of the type (4), and gives the formula (5) without determining the numerical value of the constant  $A$ . Langevin's theory includes both these types of interaction of an ion and a molecule, and can thus be used when both are operative at the same time.

## II. CALCULATION OF $A$ AS A FUNCTION OF $\lambda$ .

The course of the calculation of  $A$  as a function of  $\lambda$  is mapped out in Langevin's paper, but it seems advisable to give it in greater detail in order to facilitate any checking that may be necessary in future.

The quantity  $A$  is given by  $3/16Y$ , where

$$Y \equiv \int_0^{\infty} y e^{-z^2} z^4 dz, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and

$$y \equiv \int_0^{\pi} \cos^2 \theta \, d(\beta^2). \quad . \quad . \quad . \quad . \quad . \quad (13)$$

In these expressions

$$z = V \left( \frac{hmM}{m+M} \right)^{\frac{1}{2}}$$

where  $V$  is the relative velocity of the ion and molecule before the encounter,  $h^{-1} = 2kT$ , where  $k$  is the ordinary gas constant,  $\pi - 2\theta$  is the angle through which the relative path is deflected by the encounter, and  $\beta^2$  is a variable connected with  $\theta$  by an equation obtained from the dynamics of the encounter, viz.:—

$$\theta = (2\beta^2)^{\frac{1}{2}} \int_0^{x_1} \frac{dx}{(1 - 2\beta^2 x^2 + x^4)^{\frac{1}{2}}}. \quad . \quad . \quad . \quad . \quad (14)$$

In (14)  $x_1$  is the least root of the denominator, if it exists, and is less than  $(\lambda z)^{-\frac{1}{2}}$ , and  $x_1$  is equal to  $(\lambda z)^{-\frac{1}{2}}$  if this is not the case. There are therefore three cases to consider :

(i.) When  $\beta > 1$ , so that  $x_1$  is given by

$$x_1^2 = \beta^2 - \sqrt{(\beta^4 - 1)}, \quad . \quad . \quad . \quad . \quad (15)$$

and  $x_1$  so determined is less than  $(\lambda z)^{-\frac{1}{2}}$ . The relative orbit has then an apse at a distance from the centre of the ion greater than  $\sigma$ , so that no collision can occur.

(ii.) When  $\beta > 1$ , but  $x_1 > (\lambda z)^{-\frac{1}{2}}$ . In this case the apse is at a distance from the centre of the ion less than  $\sigma$ , so that an elastic collision does occur.

(iii.) When  $\beta < 1$ . In this case there is no apse, so that a collision is bound to take place, and then  $x_1 = (\lambda z)^{-\frac{1}{2}}$ .

The integral (14) can be reduced in all cases by trigonometrical substitution to forms which enable  $\theta$  to be expressed in terms of elliptic functions :

(i.) Put  $2\beta^2 = \sin \alpha + \operatorname{cosec} \alpha$ ,  $x = (\sin \alpha)^{\frac{1}{2}} \sin \phi$ , and then

$$\begin{aligned} \theta &= \sqrt{1 + \sin^2 \alpha} \int_0^{\frac{\pi}{2}} \frac{d\phi}{(1 - \sin^2 \alpha \sin^2 \phi)} \\ &= \sqrt{1 + \sin^2 \alpha} K\left(\frac{\pi}{2}, \alpha\right), \end{aligned}$$

using the ordinary notation for elliptic integrals.

(ii.) With the same substitution for  $\beta^2$  and  $x$ , the upper limit  $\phi_1$  of the integral is given by

$$\sin \phi_1 (\sin \alpha)^{\frac{1}{2}} = (\lambda z)^{-\frac{1}{2}}, \quad \dots \dots (16)$$

so that

$$\theta = \sqrt{1 + \sin^2 \alpha} K(\phi_1, \alpha).$$

(iii.) The substitutions  $\beta^2 = \cos 2\gamma$ ,  $x = \tan \frac{1}{2}\phi$ , reduce the integral (14) to

$$\theta = \frac{1}{2} \int_0^{\phi_1} \frac{d\phi}{(1 - \cos^2 \gamma \sin^2 \phi)^{\frac{1}{2}}} = \frac{1}{2} K(\phi_1, \frac{\pi}{2} - \gamma)$$

where  $(\lambda z)^{-\frac{1}{2}} = \tan \frac{1}{2}\phi_1$  and  $\lambda z > 1$ .

When  $\lambda z < 1$ , we write  $x = \cot \frac{1}{2}\phi$ , and then

$$\begin{aligned} 2\theta &= 2 \int_0^{\frac{\pi}{2}} \frac{d\phi}{(1 - \cos^2 \gamma \sin^2 \phi)^{\frac{1}{2}}} - \int_0^{\phi_2} \frac{d\phi}{(1 - \cos^2 \gamma \sin^2 \phi)^{\frac{1}{2}}} \\ &= 2K\left(\frac{\pi}{2}, \frac{\pi}{2} - \gamma\right) - K\left(\phi_2, \frac{\pi}{2} - \gamma\right) \end{aligned}$$

and  $\phi_2$  is given by  $(\lambda z)^{-\frac{1}{2}} = \cot \frac{1}{2}\phi_2$ .

The calculation of  $\theta$  from (14) has now to be considered from the point of view of the values of  $\lambda z$ . We then have the following table which, except for slight changes in



notation and the correction of two misprints, is copied from Langevin's paper :—

*First Type.*  $z\lambda \equiv \operatorname{cosec} \epsilon > 1$ .

$$\beta < 1, 2\theta = \sqrt{(2 \cos 2\gamma)} K\left(\phi_1, \frac{\pi}{2} - \gamma\right).$$

$$\beta^2 \equiv \frac{1}{2}(\sin \alpha + \operatorname{cosec} \alpha) > 1 \quad \left\{ \begin{array}{l} 0 < \alpha < \epsilon, \\ \theta = \sqrt{(1 + \sin^2 \alpha)} K\left(\frac{\pi}{2}, \alpha\right). \\ \epsilon < \alpha < \frac{\pi}{2}, \\ \theta = \sqrt{(1 + \sin^2 \alpha)} K(\phi_1, \alpha). \end{array} \right.$$

*Second Type.*  $z\lambda < 1$ .

$$\beta < 1, 2\theta = \sqrt{(2 \cos 2\gamma)} \left[ 2K\left(\frac{\pi}{2}, \frac{\pi}{2} - \gamma\right) - K\left(\phi_2, \frac{\pi}{2} - \gamma\right) \right].$$

$$\beta^2 = \frac{1}{2}(\sin \alpha + \operatorname{cosec} \alpha) > 1, \theta = \sqrt{(1 + \sin^2 \alpha)} K\left(\frac{\pi}{2}, \alpha\right).$$

The calculation of  $y$  from (13) for the second type ( $z\lambda < 1$ ) is fairly straightforward, both for  $\beta > 1$  and  $< 1$ . The values of the elliptic integrals were taken from Legendre's Tables, careful interpolation being necessary in dealing with the incomplete integrals.

We write

$$y = \int_0^\infty \cos^2 \theta d(\beta^2) = \int_0^1 \cos^2 \theta d(\beta^2) + \int_1^\infty \cos^2 \theta d(\beta^2).$$

The first integral, putting  $\beta^2 = \cos 2\gamma$ , is equal to

$$2 \int_0^{\frac{\pi}{4}} \cos^2 \theta \sin 2\gamma d\gamma,$$

and the second integral, putting  $2\beta^2 = \sin \alpha + \operatorname{cosec} \alpha$ , is equal to

$$\frac{1}{2} \int_0^{\frac{\pi}{2}} \frac{\cos^3 \alpha}{\sin^2 \alpha} \cos^2 \theta d\alpha.$$

The intervals in the numerical integration for  $\gamma$  were taken at  $2^\circ$  from  $4^\circ$  to  $45^\circ$ , and those for  $\alpha$  at  $4^\circ$  from  $4^\circ$  to  $80^\circ$ . At the limits of the integrals special precautions had of necessity to be taken, and the corresponding series for the elliptic integrals had to be used.

As regards the calculations of the first type ( $z\lambda > 1$ ) the real difficulty arises when  $\beta > 1$ , and  $\frac{\pi}{2} > \alpha > \epsilon$ . It was found best to take  $\phi_1$  defined by (16) as the independent variable, so that

$$\int_{\epsilon}^{\pi} \cos^2 \theta \frac{\cos^2 \alpha}{\sin^2 \alpha} d\alpha = \frac{1}{\sin \epsilon} \int_{\phi_0}^{\frac{1}{2}\pi} \cos^2 \theta \sin^2 \phi_1 \left(1 - \frac{\sin^2 \epsilon}{\sin^4 \phi_1}\right) d\phi_1,$$

where

$$\sin \phi_0 = (\sin \epsilon)^{1/2}. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

In carrying out the numerical integration for  $y$ , Weddle's rule for six equal intervals was used, and also the method of differences\*. It was found that Simpson's rule was quite unreliable if 5 figure accuracy was to be aimed at in the value of  $y$ .

The results of the calculation for  $y$  for  $z\lambda \leq 1$  were as follows:—

TABLE I.

$z\lambda \rightarrow$	0.	$\frac{1}{8}$ .	$\frac{1}{4}$ .	$\frac{1}{2}$ .	$\frac{3}{4}$ .	$\frac{1}{2}$ .	$\frac{3}{4}$ .	1.
$(\beta < 1)$	·44893	·42396	·41321	·39869	·39173	·38176	·37360	·37046
$y$ $(\beta > 1)$	·10366	·10366	·10366	·10366	10366	·10366	·10366	·10366
$y$	·55259	·52762	·51687	·50235	·49539	·48542	·47726	·47412

For  $z\lambda \geq 1$  the values of  $y$  are given in Table II.

TABLE II.

$z\lambda \rightarrow$	1.	1·155	1·333	2.	3.	4.	6.	8.
$y$ $(\beta < 1)$	·37046	·37050	·39471	·53632	·67620	·75377	·83457	·87543
$y$ $(\beta > 1)$	·10366	·10079	·08046	·03560	·11354	·27405	·68313	1·13747
$y$	·47412	·47129	·47517	57192	·78974	1·02782	1·51750	2·01290

\* Cf. D. Gibb, 'Interpolation and Numerical Integration,' Edinburgh Mathematical Tracts, No. 3.

In the final calculation of  $Y$  from (12) two methods were available, either to choose a series of values of  $\lambda$  and then to use numerical integration, or to try to express the results in Tables I. and II. in algebraic form, and then to use tables of Gamma functions for the final integration. The second method was adopted in order to avoid lengthy tabulations, and it did, I think, justify its choice.

If we write  $t$  for  $z\lambda$ , the entries in each table have to be taken in two portions, giving the following expressions:—

$$(0 < t < \frac{1}{4}), y = 0.55259 - 0.10236t + 0.00376t,$$

$$(\frac{1}{4} \leq t < 1), y = 0.53180 - 0.14784t + 0.13016t^2 - 0.04000t^3,$$

$$(1 \leq t \leq 2), y = 0.66029 - 0.32816t + 0.14199t^2,$$

$$(2 \leq t < \infty), y = \frac{1}{4}t + \frac{0.10014}{t} + \frac{0.17487}{t^3}.$$

The approximation  $\frac{1}{4}t$  corresponding to the case of elastic collisions is a useful check on the values of  $y$  for large values of  $t$ .

Finally, the values of  $\lambda$  were taken at intervals of 0.1 from 0 to 4, and the integrals were calculated by means of Karl Pearson's Tables of the Incomplete Gamma Function. The results are given in Table III.

The errors in the calculation of  $A$  arise from the expressions for  $y$  as algebraic functions of  $t$  for certain ranges of the latter variable. These errors are estimated to be possibly as much as 1 in 1250 for the range  $0 < t < \frac{1}{4}$ , 1 in 700 for the range  $\frac{1}{4} \leq t \leq 2$ , and 1 in 6000 from  $t = 2$  onwards. The resulting error in  $A$  is then calculated to be less than 1 in the third place of decimals from  $\lambda = 0.1$  to 1.1, and to be less than 1 in the fourth place of decimals for values of  $\lambda \geq 2$ .

The curve of  $A$  as a function of  $\lambda$  follows that given by Langevin very closely, and confirms the existence of a maximum value at about  $\lambda = 0.6$  for which there does not appear to be any obvious physical interpretation. It indicates that when  $(K - 1)$  is given, there is a certain value of  $\sigma$  for which the mobility is a maximum. On the other hand, Table III. shows that  $\lambda A$  increases steadily to the limiting value 0.75, so that when  $\sigma$  is given the mobility (*cf.* eqn. (7)) steadily increases as the effect of the attractive forces diminishes, as we should expect.

It is interesting to note that the expansion of  $A$  in the neighbourhood of its value when  $\lambda = 0$  is

$$A_0 + B\lambda^2 + \dots,$$

so that  $dA/d\lambda$  is infinite when  $\lambda = 0$ .

TABLE III.

$\lambda$	A.	$A\lambda$	$\lambda$	A.	$A\lambda$
0.0	·5105	·0000	2.1	·3370	·7077
0.1	·5488	·0549	2.2	·3236	·7119
0.2	·5648	·1130	2.3	·3111	·7155
0.3	·5756	·1727	2.4	·2994	·7186
0.4	·5836	·2334	2.5	·2886	·7215
0.5	·5886	·2943	2.6	·2784	·7238
0.6	·5904	·3542	2.7	·2689	·7260
0.7	·5878	·4115	2.8	·2599	·7277
0.8	·5796	·4637	2.9	·2515	·7293
0.9	·5662	·5096	3.0	·2436	·7308
1.0	·5483	·5483	3.1	·2362	·7322
1.1	·5277	·5805	3.2	·2292	·7334
1.2	·5057	·6068	3.3	·2226	·7346
1.3	·4834	·6284	3.4	·2163	·7354
1.4	·4614	·6460	3.5	·2104	·7364
1.5	·4402	·6603	3.6	·2048	·7373
1.6	·4201	·6722	3.7	·1994	·7378
1.7	·4011	·6819	3.8	·1944	·7387
1.8	·3834	·6901	3.9	·1895	·7391
1.9	·3668	·6969	4.0	·1849	·7396
2.0	·3514	·7028			

It is of interest to see how far Sutherland's formula, which applies only to weak attractive forces, is in error in this case, which corresponds to the diffusion of one gas into another when the molecules are spheres with a surrounding field of attractive force, varying inversely as the fifth power of the distance. The expression for A in our notation is \*

$$\frac{3}{4\lambda} \frac{1}{[1 + 0.2011/\lambda^2]} \quad \dots \quad (18)$$

For example,  $\lambda = 2$  gives  $A = .3562$  instead of  $.3514$ ,  $\lambda = 2.5$  gives  $.2907$  instead of  $.2886$ , and  $\lambda = 3$  gives  $.2445$  instead of  $.2436$ . Thus Sutherland's approximation is in error by less than 1 per cent. for  $\lambda = 2.5$ , and by less than 1.4 per cent. when  $\lambda = 2.0$ . Further, the values calculated from James' formula are all in excess of the correct values in accordance with his result that the next term in the series in  $\lambda^{-2}$  in the denominator of (18) is positive.

\* Cf. James, *loc. cit.* p. 454.

### III. APPLICATION TO THE CALCULATION OF MOBILITIES.

#### 1. *Physical Data of the Theory.*

The quantities on which the theoretical determination of the mobility of an ion depends are the distance  $\sigma$  between the centres of the colliding ion and molecule, the masses  $M$  and  $m$ , the density  $\rho$  of the gas, and the value of  $K-1$  for the gas. There is a fair measure of agreement in the results given by different methods for the statical value of  $(K-1)$ , which has been taken for a temperature of  $15^\circ \text{C}$ . The values of the density  $\rho$  have been taken from Kaye and Laby ('Physical Constants,' p. 26), and have similarly been reduced to a temperature of  $15^\circ \text{C}$ . These values are given in the following table:—

TABLE IV.

Gas	$(K-1) \times 10^4$ at $15^\circ \text{C}$ .	$\rho \times 10^3 (\text{gms./cm.}^3)$ at $15^\circ \text{C}$ .
Air.....	543	1.226
Argon .....	529	1.688
Helium .....	66	0.1689
$\text{H}_2$ .....	250	0.0852
$\text{O}_2$ .....	491	1.355
$\text{CO}$ .....	656	1.185
$\text{CO}_2$ .....	898	1.875
$\text{NH}_3$ .....	7450	0.7306
$\text{SO}_2$ .....	8760	2.774

In order to determine the value of  $\sigma$ , we must know the values of the radii  $s$  and  $s'$  of the molecule and ion respectively, and this involves a definite assumption as to their constitution. The most general procedure would be to consider a neutral molecule as the seat of both repulsive and attractive forces, and to consider in addition the attractive forces between the ion and the neutral molecule. Unfortunately the theory as at present developed does not allow of such a general treatment. The method of simplifying the problem that immediately suggests itself is to take the repulsive force as equivalent to that given by collision with an elastic sphere of radius  $s_0$ , the so-called "kernel" of the molecule. We are then left with the attractive force due to cohesion, and that due to the electrical field of the charged ion, and here again the proper method is to combine these into a single attractive force, and to separate out the

constituent parts in the application to any particular case. This method, due to Sutherland, has difficulties of its own of a mathematical character, and must be left over for further consideration.

Another possible method is to take the effect of the attractive and repulsive forces of the neutral molecule as equivalent to that given by an elastic sphere of radius  $s$ , determined from measurements of viscosity, and given by Jeans \* for a temperature of  $0^\circ \text{C}$ . This method is clearly very unsatisfactory and most of the difficulties we shall meet with may be traced to its use, but it is the best that can be adopted in the present state of our knowledge, and these values of the radius  $s$  of the molecule will be used in the numerical calculations given in this paper. The value of  $s$  will depend on the temperature, and the value taken in all cases is that corresponding to a temperature of  $15^\circ \text{C}$ ., since the values of  $(K-1)$  and  $\rho$  have also been taken for this temperature.

The effect of the attractive force between the ion and the neutral molecule given by (4) is then calculated from Langevin's theory as an effect superposed on that due to the attractive and repulsive forces of the molecule itself. This is a further definite assumption, and one which it is impossible to justify, either physically or mathematically. There appears to be no reason why the effect of the collision of a charged and a neutral molecule should be represented by the same value of the "effective" radius  $s$  as in the case of the collision of two neutral molecules.

We are now in a position to calculate the value of  $\lambda$  from (6), and to determine the mobility from (5), in which the numerical values must be divided by 300 in order to express the results in cm./sec. per volt/cm.

## 2. Mobility of a Mono-Molecular Ion.

The first case we shall consider is that in which the ion is a single molecule, positive or negative, when  $M = m$ , so that

$$k = \frac{A \sqrt{2}}{\sqrt{\rho(K-1)}}, \quad \dots \quad (11)$$

where we have taken no account of the Chapman-Enskog correcting factor, and we shall then have the following table :—

\* Jeans, 'Dynamical Theory of Gases,' 3rd edition, p. 288.

TABLE V.  
Mono-Molecular Ion.

Gas.	$\lambda$ .	A.	k.
Air .....	·626	·590	3·41
Argon .....	·605	·590	2·95
Helium .....	·622	·590	26·6
H <sub>2</sub> .....	·490	·588	19·0
O <sub>2</sub> .....	·614	·590	3·38
CO .....	·580	·590	3·16
CO <sub>2</sub> .....	·733	·585	2·12
NH <sub>3</sub> .....	·221	·567	1·15
SO <sub>2</sub> .....	·331	·578	0·545

These values are far larger than those given by the experiments, and of course there is no difference in the mobility of the positive and negative ion on this assumption of a single mono-molecular ion.

According to this theory these are maximum values for the mobility. If the higher values obtained in some experiments are substantiated, there must be free electrons present, and the higher mobilities must be due to stable concentrations of electrons and molecules in different quantities.

### 3. *Mobility of a Clustered Ion in its own Gas.*

It has therefore been suggested that the smaller mobility of the ion is due to the fact that the molecules form a cluster round the ion, and that we have to deal with the diffusion of the clustered ions in the field of the other molecules. The condition that such a clustering shall take place is that the potential energy of the molecule in contact with the ion shall be greater than the average kinetic energy of their relative motion. The ratio of these two energies is

$$\frac{(K-1)e^2}{8\pi N\sigma^4} \bigg/ \left(\frac{3}{2}kT\right) = \frac{(K-1)e^2}{12\pi p\sigma^4} = \frac{2}{3\lambda^2},$$

where  $k$  is the ordinary gas constant\*.

The ratio  $2/3\lambda^2$  may be called the clustering coefficient, and we see that it will be greater than unity if  $\lambda$  is less than 0·8165, which is the case for all the gases given in Table V.

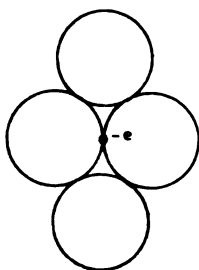
\* It should be realized that this deduction of the condition of clustering belongs to a different order of ideas from that of strict kinetic theory. According to the latter there can be no such clustering, as two molecules or ions will always separate after an encounter. Hence those conclusions given in this paper which depend on this clustering condition may be liable to modification.

The positive ion will then be represented, following Langevin, as a sphere of radius  $s$  with a layer of spheres, 12 in number, clustered round it. This makes  $M = 13m$ , and the distance  $\sigma$  between the centres of a molecule and the clustered ion at collision is then practically  $4s$ , though the average distance would be slightly less than this.

It is more difficult to form a satisfactory representation of a clustered negative ion. Assuming that the basis of the cluster is a free electron, Langevin takes the clustered ion as a sphere of radius  $2s$ , so that  $\sigma = 3s$ , and takes the masses of the molecule and ion as proportional to their volumes, which makes  $M = 8m$ .

It is desirable for certain purposes to make this representation more definite, and we may suppose that initially two molecules will attach themselves to the free electron, forming two spheres in contact, and that further molecules, 5 in number, will cluster round these two in their plane of symmetry, as in the figure representing a section of the cluster.

Fig. 1.



In this case  $M = 7m$ , and the average radius of this cluster can be calculated by the methods introduced by Rankine\*, taking the cluster as equivalent to an ellipsoid of revolution, and calculating its mean collision area.

In the remainder of this section we shall consider the case of an ion in a gas composed of its own molecules. The cluster is therefore formed of these molecules, and the collisions of the clustered ion are with other molecules of the gas. The results may therefore be taken as applying to a dry gas only; the effect of the presence of water vapour will be considered in the next section.

\* Rankine, Proc. Roy. Soc. A, xcvi. p. 360 (1921).



The following table gives the results of calculation as applied to the positive ion:—

TABLE VI.  
Positive Clustered Ion.

Gas.	$\lambda$ .	A.	$k$ .
Air.....	2.504	.288	1.37
Argon .....	2.420	.297	1.23
Helium .....	2.488	.290	10.8
H <sub>2</sub> .....	1.960	.358	8.45
O <sub>2</sub> .....	2.456	.293	1.40
CO.....	2.320	.309	1.37
CO <sub>2</sub> .....	2.032	.259	0.78
NH <sub>3</sub> .....	0.884	.568	0.84
SO <sub>2</sub> .....	1.324	.478	0.33

It will be seen that the values of  $\lambda$  are all greater than 0.816, so that no further clustering will take place.

It should also be noticed that in most of the cases the value of  $\lambda$  is so large that equation (8) is applicable, so that the mobility is independent of the value of  $(K-1)$ , and it could have been calculated directly from this equation. Hence, in the case of positive ions, the attractive forces are instrumental in forming the cluster, the mobility of which depends then largely on its radius.

TABLE VII.  
Negative Clustered Ion.

Gas.	$\lambda$ .	A.	$k$ (Langevin's Representation).	(Cluster as in fig. 1.)
Air .....	1.408	.460	1.99	2.04
Argon .....	1.363	.469	1.76	1.79
Helium .....	1.400	.461	15.6	16.1
H <sub>2</sub> .....	1.102	.527	12.7	13.0
O <sub>2</sub> .....	1.382	.465	2.02	2.07
CO .....	1.305	.482	1.93	1.98
CO <sub>2</sub> .....	1.649	.411	1.11	1.14
NH <sub>3</sub> .....	0.497	.588	0.89	—
SO <sub>2</sub> .....	0.745	.584	0.41	—

We may in a similar way calculate the mobility of a clustered ion, and here it is of interest to give some results, both for Langevin's rough representation, and for the more

definite clustering shown in fig. 1. It will be seen that these differ very slightly, a result which may be taken as suggesting that the geometrical form of the cluster will have very little effect on the mobility, which naturally gives a statistical average over a large number of clusters.

Theoretically, further clustering should take place in the case of  $\text{NH}_3$  and  $\text{SO}_2$ , since  $\lambda < 0.816$ , but it is not worth while to deal with these cases in further detail. The values of  $k$  correspond to the values of  $\lambda$  given in the table.

Other possibilities in the way of representing the geometry of a clustered negative ion obviously suggest themselves, but it is hardly desirable to consider them at this stage of the inquiry.

#### IV. COMPARISON WITH EXPERIMENT.

##### 1. Mobilities of Ions in Dry Gases.

The results given in the previous section relate to fully-clustered ions, and cannot therefore be taken as applying to experiments intended to give values for the mobility of partially-clustered ions which correspond to a position of minimum energy, but not in a state of greatest stability.

We have the following results, in which the calculated values for the mobilities of positive and negative ions, denoted by  $k+$  and  $k-$  respectively, are taken from Tables VI. and VII. :—

TABLE VIII.

##### Positive Clustered Ion.

Gas.	$k+$ (Theoretical).	$k+$ (Experimental).
Air .....	1.37	1.40, mean value, Kaye and Laby, p. 95.
Argon .....	1.23	1.37, Franck (1910).
Helium .....	10.8	5.09, Franck and Pohl (1907).
$\text{H}_2$ .....	8.45	5.4, Haines (1916); 5.33, Lattey and Tizard (1912); 5.8, Chattock and Tyndall (1910).
$\text{O}_2$ .....	1.40	1.33, mean value, Kaye and Laby.
$\text{CO}$ .....	1.37	1.10, Wellisch (1909).
$\text{CO}_2$ .....	0.78	0.82, mean value, Kaye and Laby.
$\text{NH}_3$ .....	0.84	0.74, Wellisch (1909).
$\text{SO}_2$ .....	0.33	0.44, Wellisch (1909).

TABLE IX.

## Negative Clustered Ion.

Gas.	$k-$ (Theoretical).	$k--$ (Experimental).
Air.....	1.99	1.78, mean value, Kaye and Laby; 2.15, Loeb (1923).
Argon.....	1.76	1.70, Franck (1900).
Helium .....	15.6	6.31, Franck and Pohl (1907).
H <sub>2</sub> .....	12.7	7.9, Haines (1916); 8.12, Lattey and Tizard (1912); 7.6, Chattock and Tyndall (1910).
O <sub>2</sub> .....	2.02	1.82, mean value, Kaye and Laby.
CO .....	1.93	1.14, Wellisch (1909).
CO <sub>2</sub> .....	1.11	1.01, Kovarik (1910); 1.05, Lattey and Tizard (1912).

The agreement in both cases is fairly satisfactory, except in the case of the light gases Helium and Hydrogen. It is, indeed, more satisfactory than we have a right to expect, considering the nature of the assumptions made in the course of the calculation. In view of the disagreement in the case of the light gases, it is possible that such agreement as there is in the other cases may be quite accidental.

## 2. *The Effect of Water Vapour.*

It has been suggested that, since free electrons are present in many of the gases considered above when in a highly purified state and these would naturally have very high mobilities, the experimental values given above for negative ions are really the mobilities of water-vapour clusters in the presence of the molecules of the gas itself. It is of interest to consider this question on the basis of the method of calculating mobilities given in this paper.

Assuming such a cluster is possible, we require for the calculation of the mobility the value of the effective radius  $s$  of a water-vapour molecule. Taking the value  $97 \times 10^{-8}$  c.g.s. units for the viscosity of water vapour at  $15^{\circ}$  C., as given in Kaye and Laby, p. 31, which agrees well with more recent values, we find that  $s = 2.24 \times 10^{-8}$  cm.

In the case of Air it is then found that if the ion is clustered with water-vapour molecules instead of air molecules, the value of  $k+$  is reduced from 1.37 to 1.15, and the value of  $k-$  from 1.99 to 1.68. In the case of H<sub>2</sub> the presence of water vapour in sufficient quantities to allow of the formation

of clusters of water vapour round the  $H_2$  ions will make the mobility of the positive ion in  $H_2$  equal to 4.85, and that of the negative ion equal to 7.37, so that the suggestion does lead to better agreement between theory and experiment in this case.

Unfortunately, the same is not true in all cases. The mobility of an ion in slightly damp gas, so that it is clustered with water-vapour molecules, in the presence of molecules of its own gas as compared with the mobility in dry gas, depends according to the method of calculation only on the difference in values of the radii  $s$  of a water-vapour molecule and that of a molecule of the dry gas. Hence, in the case of  $CO_2$ , where  $s$  has the value  $2.31 \times 10^{-8}$  cm., and is therefore greater than the radius of a water-vapour molecule, we should expect a decrease in mobility when the gas is dried, which is contrary to the experimental results.

### 3. Mobilities of Ions in Foreign Gases.

The important experimental fact that the mobility of the positive ion depends only on the gas into which it is introduced has already been mentioned in I. 2 above, and has been used there to show the necessity of a cluster. If this is so, and the recent experiments of Tyndall and Grindley\* seem to leave very little room for doubt on the point, then, as has been shown by J. J. Thomson† in connexion with the limiting cases of Langevin's theory discussed by him, it leads to conclusions which are of great theoretical significance. From the general formula (5) it follows from this experimental result that  $A$  must be independent of the nature of the ion. Since  $A$  is a function of  $\lambda$ , then either  $A$  must vary very slowly with  $\lambda$ , or else  $\sigma$  must be practically the same for all ions clustered with molecules of the same gas. The first possibility means that  $A$  must have values near its maximum, which corresponds to  $\lambda = 0.6$  approximately, and this would mean according to the theory that further clustering would take place. Hence it follows that the radius of an ion fully clustered with molecules of a given gas must be practically independent of the nature of the ion.

The method of calculating the mobility as used in this paper leads to results quite at variance with the experimental fact we are considering. Thus, in the experiments of

\* Tyndall and Grindley, *Phil. Mag.* xlviii. p. 711 (1924).

† J. J. Thomson, *loc. cit.*

Tyndall and Grindley referred to, a  $\text{CO}_2$  ion and a  $\text{H}_2$  ion in air are shown both to have the same mobility as that of an air ion in air. Assuming a cluster of air molecules in each case the values of  $\sigma$  (*cf.* Jeans, *op. cit.* p. 288) are in the ratios  $2.31 + 3 (1.87) : 1.36 + 3 (1.87) : 1.87 + 3 (1.87)$  or  $7.92 : 6.97 : 7.48$  in the three cases. Since the value of  $\lambda$  is large, equation (8) is applicable, and it follows that the substitution of a  $\text{CO}_2$  ion for an air ion lowers the mobility in the ratio  $(7.92)^{-2}$  to  $(7.48)^{-2}$  or 0.89, and that the substitution of a  $\text{H}_2$  ion will raise it in the ratio 1.15. These differences of 11 and 15 per cent. are quite outside the possible errors of the experiment.

## V. GENERAL DISCUSSION OF THE THEORY.

The considerations given in IV. 2 and IV. 3 show that, in spite of the results of IV. 1, the method of calculating the mobilities is not very satisfactory. It is clear, in fact, that we cannot use the "effective" radius  $s$  of the molecule for this purpose. The fields of force which are represented by this radius will interpenetrate, and will possibly be altered in magnitude, owing to the additional attractive force exerted by the ion on the molecule, and it will be necessary to find some means of determining the size and shape of the clusters before much progress can be made.

It is possible that the fields will interpenetrate so much that the clustering is of a more extensive character than that so far contemplated. This would result in the size of the cluster being practically independent of the size of the ion at its centre, but a numerical estimate will have to be provided before any definite statement can be made.

The above remarks do not apply to the calculated values for the mobility of a mono-molecular ion given in Table V., since there is no question of any clustering in this case, so that the numbers given there remain the estimated maximum values.

In this connexion it is important to realize the limitations of the theory of mobility as given in this paper. No attempt has been made to consider in detail how the clustering takes place, or what types of cluster are likely to occur; nor does the theory necessarily apply when there are free electrons present, as has been at times suggested in order to account for certain experimental results. A discussion of some of

these questions from the theoretical side has been given by J. J. Thomson \*, based on the ideas associated with the older type of kinetic theory.

For example, the experiments of Erikson † have shown that there are two types of positive ion, an initial ion of about the same mobility as the negative ion, and a final ion of much smaller mobility. The only way of accounting for this fact on the present theory would appear to be to assume that initially the positive cluster is of the same type as that given in fig. 1, in which  $+e$  takes the place of  $-e$  in the figure, and that this cluster changes into one in which the positive ion becomes the centre of a group of molecules surrounding it. The theory does not enable us to say why these two types of ion exist. Erikson's explanation, since it is based on Wellisch's equations for the mobility, cannot, for the reasons given in I. 2 above, be considered satisfactory.

Again, in the case of the negative ion, some evidence has been given of the existence of mobilities higher than that calculated above in III. 3. We may therefore consider in the case of Air what would be the mobilities of negative ions obtained by building up ions of one, two, . . . molecules in succession. The mobility of the mono-molecular ion is 3.41, while that of the fully-clustered ion is 1.99. Other values are obtained by considering the possible geometrical representations of partially-clustered ions. The case of two spheres which touch and have the electron at their point of contact gives a value for the mobility of 2.85, while that of three spheres touching each other and having the electron at their geometrical centre makes the mobility equal to 2.43. The case of four spheres touching each other, and therefore having their centres at the corners of a tetrahedron, leads to the value 1.90, almost the same as that of a fully-clustered ion.

It is not desirable to place any great emphasis on these numerical values for the reason given at the beginning of this section, and owing also to the rough representation of clustered ions on which they are based. They have been added here in order to complete the review given in this paper of the relation of the results of this method of calculating mobilities to the results given by experiment.

\* J. J. Thomson, *Phil. Mag.* (6) xlvii. p. 337 (1924).

† Erikson, *Phys. Rev.* xx. p. 117 (1922).

## SUMMARY AND CONCLUSIONS.

1. The paper has been written in order to recall attention to the theory of ionic mobility given by Langevin in 1905, and to consider the applications of the theory to problems in this subject. This is the only theory of mobility which is satisfactory from a theoretical point of view, since it is based on the rigorous mathematical investigations introduced into the kinetic theory of gases by Maxwell and Boltzmann.

2. A recalculation has been given of the numerical portion of Langevin's paper. This confirms the existence of a maximum mobility for a particular value of the distance between the centres of the ion and molecule at collision, the magnitude of the attractive forces being given.

3. Calculations of the mobility of several gases at atmospheric pressure are made on various assumptions, more or less reasonable, as to the size and shape of the molecules and clusters involved.

4. It is shown that the application of the theory as at present developed fails to account for some of the more fundamental experimental results, in particular for the fact that the mobility of a positive ion depends only on the nature of the gas through which it is diffusing under the influence of the external field.

5. The paper is therefore mainly of the nature of a preliminary investigation, and further work will be necessary before the application of the theory to the calculation of mobilities and the comparison of the results with experiment can be dealt with in a satisfactory manner.

My thanks are due both to Dr. J. E. Lennard-Jones, who is working on the subject from another point of view, and to Prof. A. M. Tyndall, with whom I have had the opportunity of discussing certain points connected with the theoretical and experimental side of the subject respectively.

In connexion with the numerical work of Section II., I should like to acknowledge the valuable assistance I have received from Miss D. L. Holland and Miss N. M. Hunt.

The University of Bristol.  
August 1925.

**XI. Mechanical Models for the Zeeman Effect.** By C. G. DARWIN, M.A., F.R.S., Tait Professor of Natural Philosophy in the University of Edinburgh \*.

**ABSTRACT.**

The field of applicability is discussed of mechanical models for spectral lines (§ 2).

The principles are explained (§ 3) and the actual form is given (§ 10, 11) of a simplification of Voigt's model of the D lines, which invests it with much greater physical significance.

A curious theorem is found concerned with the magnetic gyration of light (§ 8). Provided the assumed type of model is correct, the gyration of light of frequency far distant from the lines of a multiplet should correspond to a normal Zeeman effect, and should show no trace of the anomalous effect no matter how weak the field or how complex the multiplet.

It is shown (§ 9) that some types of multiplet cannot be represented by the simple form of the model.

An attempt is made to construct a model for the triplet (§§ 14-15). The result satisfies all the known properties, but no success has been attained in finding a simple form such as would suggest a basis of physical reality.

The remaining sections are concerned with technical principles of the theory of vibrations.

In spite of the rather striking success with the doublet, the general verdict seems probable that though models can always be devised for any type of line, they will not in general possess the simplicity which would make them useful.

**1. Introduction.**

**I**N the last few years the theory of the Zeeman effect has undergone enormous developments with the help of quantum principles, and it is hardly too much to say that the position and intensity of every line are now completely known. But there remains outstanding the question of how a substance will react to light of frequency different from its own lines. In dealing with the refraction and magnetic rotation of light our guiding principle is the Lorentz theory of electrons, and to use this we must have some sort of mechanical model for the atom. In addition to the simple elastically bound electron of Lorentz, there exists one other model

\* Communicated by the Author.



which was devised by Voigt\* to describe the behaviour of the D lines of sodium. It seemed to me that, in view of the greatly increased knowledge we now possess, it would be worth while to re-examine the subject and to see whether other models of the same type could be usefully made. The principles of which we shall treat were I think mostly contained in Voigt's own work, but in some respects he was aiming in wrong directions through insufficient experimental information. Moreover, there is no avoiding the fact that Voigt's papers make exceedingly difficult reading, and it may be doubted if they have been much studied for that reason ; so a new development of the theory may have some value.

To use a mechanical model at all we must, of course, have some connecting link between the classical and the quantum theories. Though the underlying principles are still quite unknown, such a link can be made in a manner described by Ladenburg † and later and with a fuller theory by Kramers ‡. With these rules it is quite possible to calculate the dispersion of any light passing through a substance, when we know the frequencies, intensities, and polarizations of the lines it emits in any strength of magnetic field ; but Voigt's model can do much more than this, for it can derive from a fairly simple set of equations the whole behaviour of the spectrum for both weak and strong fields. In the course of the present work it was found that Voigt's model could be cast into a much simpler form, and one in which a good deal of physical significance could be seen. This gave a new direction to the work, for it seemed that the same might be possible for other types of multiplet. I am rather inclined to think that this is not so, and that it is an accident that Voigt's model embodies so many facts in such a small compass, but the algebra becomes so involved and the number of alternative choices so vast that it is by no means possible to be certain. I had the impression in starting the work that it would not be easy to find any systems which would accommodate all the known facts, for example, the behaviour in both weak and strong fields. It soon appeared, however, that the opposite would be the difficulty ; the condition for the Paschen-Back effect takes a simple and indeed rather elegant form, but is quite insufficient to determine many of the

\* Voigt, *Ann. der Phys.* vol. xli. p. 403 (1913), and vol. xlii. p. 210 (1914). Voigt's model is fully discussed by Sommerfeld, *Z. f. Ph.* viii. p. 257 (1921).

† Ladenburg, *Z. f. Ph.* vol. iv. p. 451 (1921).

‡ Kramers, 'Nature,' vol. cxiii. p. 673, and vol. cxiv. p. 310 (1924).

constants of the model. Before proceeding to the detailed theory, we must review the general question of the possibility of representing the facts of optics by means of mechanical models.

## 2. *The General Applicability of Mechanical Models.*

We are going to deal with ordinary vibrating systems and must first examine in general terms how far we may hope that they will be able to represent the facts of physics. The four main effects to be examined are dispersion (including magnetic rotation), emission, absorption, and resonance radiation, and we are starting from the opposite end from that done by the quantum theory, in that we take our system to give the dispersion correctly and then see how it will deal with the other phenomena. Since all dispersive effects are independent of intensity the equations of motion of the model must be linear, and come under a fully known theory. The model is necessarily somewhat unnatural in that, to represent a multiplet, it must have a considerable number of nearly equal frequencies. Though it is not easy to conceive of a real atom having this property, yet it does free us of one of the objections to mechanical models for spectra; for by taking the differences between the frequencies as small, we can get period equations which are linear in the frequency (and not quadratic as in the general case) and so can much more easily fit the system to the linear expressions for the frequency that occur in the quantum theory. Furthermore, this approximation very considerably simplifies the theory of the vibrations of systems containing gyroscopic terms. The model must not only have the correct natural frequencies, but each of these must have the correct "force factor," so as to describe their relative importance in reacting to the incident light.

When the model has been chosen to fit the dispersion, we have to consider what spectrum it will *emit*. The most usual way of exciting the emission of radiation is by means of electron collisions. The process is essentially one of which the quantum theory gives a good and the classical theory a bad account, and so we cannot expect that our model will represent the event very successfully. We suppose that the impact of the electron gives the various degrees of freedom certain displacements and velocities, and that it then describes free vibrations. The dispersion theory then determines the emission. In general the strengths of the various lines will depend on the initial values chosen, and we conclude that there is not, in general, a definite set of

ratios for the intensities of the members of a multiplet. We may note that there is an analogous theorem in the quantum theory. For example, the impinging electrons might all have enough energy to excite  $D_1$  but not  $D_2$ , and we should then certainly not observe the usual ratio 1 : 2. We expect that the electron velocities must be a good deal higher before this ratio is given. Taking the analogy back again, we shall show that our model will give a perfectly definite set of ratios—that determined by the dispersion—provided that there is an equipartition of energy among the degrees of freedom of the model. The question of the intensity ratios for lower velocities of impact is most interesting, but falls outside our present subject. We may note that for temperature radiation the quantum theory gives a perfectly definite answer, which will usually not be far from that given by equipartition; the conditions in a discharge tube defy precise analysis, but the velocities of the electrons are usually so high as to give practical equipartition.

If the only damping of the vibrations is due to the re-emission of electromagnetic waves, it follows by a purely thermodynamic argument that the intensity of absorption must equal that of emission. We shall see, however, that for resonance radiation some other type of damping is needed, and we are then confronted with a problem in which the balance of energy is not explicitly maintained. We shall show that whatever the damping factors, provided they are small, the absorption will follow the same rule as dispersion and emission. We shall not consider the question of the breadths of the spectral lines, and so there is no need to inquire deeper into the matter.

The question of resonance radiation is more difficult and falls more distinctly outside the competence of the classical theory. The crudest form of analogy would suppose that the incident light, having the same frequency as the natural frequency of the model, would set it into strong vibration in a phase determined by the electromagnetic damping of the model, and that the resonance radiation was the light scattered in the process. This will not do at all. For when light is scattered in this way the waves from the separate atoms are all in phase together (though perhaps out of phase with the incident light) and so the light scattered laterally is akin to the light of the sky, the intensity of which can be calculated directly from the refractive index of the air. To obtain the intense effect observed in resonance the vapour would have to have an enormous refractive index. There is no reason in the theory of dispersion why it should not have this large

index (real or complex), but that it does not is proved by the fact that there is no very strong reflexion from the surface of the vapour.

The only alternative to account for the strong scattering is to suppose that the atom is responsible for two waves. The first bears a definite phase relation to the incident of such a type that this is gradually extinguished in passing through the vapour. If this wave is associated with the ordinary electromagnetic damping factor it will represent no accumulation of energy in the atoms. To absorb energy the atom must have a further damping factor, and we must suppose that the strong scattering is produced when the atom discharges this energy at a later time and with arbitrary phase. It will be seen that this argument, though involving nothing but pure wave theory, points definitely towards the quantum way of regarding the matter, and we are forced to conclude that our mechanical model will fail to connect at all closely the absorption and the re-emission. This is confirmed by the fact that the resonance often gives rise to lines different from the exciting line, and these are immediately explained by the quantum theory. The only way of arriving at a construction for the process is to take a model having non-linear equations of motion. This will give wrong results for dispersion since the motion will not be directly proportional to the amplitude of the exciting force, and we must therefore expect that a new application of the Correspondence Principle will be necessary in order to interpret it\*. I shall not here speculate further on the subject, for a paper evidently dealing with the matter is promised shortly by Kramers and Heisenberg†.

To make use of our more limited model we must assume that the energy is absorbed in a manner that would be indicated by the dispersion—there is no need to investigate precisely the damping coefficient unless we intend to study the breadth of the spectral lines etc.—that there is some sort of reorganization in the atom, after which the energy is re-emitted, but to decide the reorganization we have to invoke the quantum theory. For example, we must simply take it as given that in sodium the excitation of  $1s-2p_1$  leads to a re-emission of that line only, while in thallium  $2p_1-1s$  leads

\* It is tempting to compare the two waves with the superposed forced and free vibrations of a system starting from rest, but the correspondence must be more complicated than this for the solution of a set of non-linear equations does not divide up into two parts in this way.

† This paper has since appeared, *Z. f. Ph.* vol. xxxi. p. 681 (1925); it is an amplification of Kramers's work (*loc. cit.*).

to a re-emission of that line accompanied by  $2p_2-1s$ , the intensity ratio being that given by the dispersion. So we must suppose that as a result of quantum arguments our model acquires certain initial values for its coordinates, and calculate the intensities from these.

### 3. *The Transformation of Voigt's Model of the D Lines.*

We shall now consider Voigt's model in general terms. He worked it out mainly by fitting it to the effect in weak fields; and found, it might be said almost by accident, that it fitted for strong fields as well. Also by taking his equations in as symmetrical a form as possible he obtained the intensities of the components in weak fields according to the following scheme:—

	$D_2$			$D_1$	
Frequency .....	$\pm\frac{2}{3}$	$\pm 1$	$\pm\frac{1}{3}$	$\pm\frac{4}{3}$	$\pm\frac{1}{3}$
Intensity .....	1	3	4	2	2
Polarization .....	$\perp$	$\perp$	$\parallel$	$\perp$	$\parallel$

In very recent developments of the quantum theory these intensities are accepted as correct; but there does not seem to be any direct verification of them from emission spectra. Until recently it was believed that the light was anisotropic and that the intensities of the components were much more nearly equal; and it is thus rather natural to take the fact that the model was ahead of theory as a confirmation of its objective reality. Though there has been no satisfactory measure of the intensities of emission, it should be observed that the values above were proved long ago by perfectly cogent though slightly indirect arguments based on the necessary connexion between refraction and emission. Thus every experiment on magnetic double refraction shows the birefringence to be proportional to the magnetic field, and this proves that the anisotropy of the atoms is also proportional to the field, and not absolute, as would be suggested by the crude form of the quantum theory. Further, the same type of argument will determine the intensities of the lines from their dispersive effect. This was done in some very fine experiments by Hansen\*, and with an accuracy sufficient to verify the above values to 10 per cent. Thus Voigt's model fits in with present theory to a very complete degree. In only one respect can it be attacked.

\* Hansen, *Ann. der Phys.* vol. xliii. p. 169 (1914).

Landé\* has recently applied Heisenberg's† method of quantizing so as to find the position of the lines for intermediate fields, and his results definitely do not agree with Voigt's. There seems to be no conclusive experimental evidence on the point. As the physics of Heisenberg's process are incompletely understood, we cannot feel full confidence that it destroys the validity of the model, but, taken in conjunction with results that will be given later, it does look as if the success of the model were rather accidental. We shall next describe the general principles of the modifications which have improved its form.

As the atom cannot be really described at all in terms of ordinary mechanics there is no use in associating very precise physical meanings with the variables of the mechanical system which acts as model. A sufficient starting point will be to set down its Lagrangian function. This is composed of four parts: the first three, kinetic energy, potential energy, and gyroscopic terms, constitute a quadratic form in the coordinates and velocities. The fourth is the "force function," which describes the connexion with the outside world; it is a bilinear form in the coordinates and the external forces. Only if the model is of this form will the equations of motion be linear, as is required if the refractive index is to be independent of the intensity.

The usual problem of vibrations starts with a known form and requires us to find the natural frequencies of the motion and their modes. Here the question is the exact opposite; we know all the natural frequencies and their intensities, and our object is to discover a simple algebraic form which can be responsible for them. This was successfully done by Voigt, and his equations of motion have an attractive type of symmetry, but the Lagrangian function from which they are derived is a very long expression if written out in full. Now in treating of the ordinary problem of vibrations a certain degree of simplicity is obtained by first reducing the kinetic and potential energies to sums of squares, and then later studying the effects of the gyroscopic terms. This form of the expression may conveniently be called the *semi-normal*, and it would not be expected to be as significant as the original form or as simple mathematically. The semi-normal form is exactly what is used in describing the anomalous Zeeman effect in weak fields, for it refers each vibration to the value it would have if there were no gyroscopic terms. Voigt has his equations of motion in this

\* Landé, *Z. f. Ph.* vol. xxx. p. 329 (1924).

† Heisenberg, *Z. f. Ph.* vol. xxvi. p. 291 (1924).

form. The first modification we shall make is to abandon it, by including product terms in the potential energy (or the kinetic), and we shall find that a great simplification results.

The second modification is quite as important, and concerns the *force function*. Voigt works with three electrons all reacting to the external field in the same way. Now the quantum theory suggests that in sodium one electron is mainly responsible for the spectrum, the rest only acting indirectly by perturbing it. Though the analogy can only be rather loose, this suggested the idea of taking only one of the degrees of freedom as affected by external electric forces and the result was found further to simplify the model. Moreover, there is direct evidence that this is a step in the right direction from some experimental work by Minkowsky\*. He finds that the absolute refractive index of sodium vapour is given by the classical theory if each atom contains one electron of ordinary charge and mass, responsible for the whole of both  $D_1$  and  $D_2$ †.

These two ideas led to very pronounced simplifications in the model, modifications which seemed to give it a much more physical meaning, and it looked possible that similar models might exist for other multiplets. There is, of course, no obvious reason why there should exist any at all, but the conspicuous success with the doublet made it well worth while to examine other cases. There even seemed to be a faint chance of constructing a general model which should contain the quantum numbers as numerical coefficients in its Lagrangian function; the algebra of the classical systems, it is true, is rather complicated, but in the only known case it was exactly equivalent to the simple arithmetic of the quantum theory. In dealing with multiplets we have an important fact of which account should be taken in the model, and this is that an ordinary multiplet can be approximately described in terms of two parameters, the frequency of its centre of gravity, and a single constant determining all the intervals between the lines. For example, in a triplet  $1s\text{--}mp$  the intervals are approximately in the ratios 1 : 2, and the intensities as 1 : 3 : 5. The semi-normal form gives

\* Minkowsky, *Ann. der Phys.* vol. lxvi. p. 206 (1921).

† The dielectric constant of Na is presumably due to a single electron, which must therefore be responsible for the whole principal series. There should thus be a small reduction to allow for the higher members of the series. Ladenburg (*loc. cit.*) shows that the dispersive effect of these lines is insignificant.

directly the frequencies of the components, and fails to bring out the arithmetical character of their intervals. It was this consideration, indeed, that suggested abandoning the semi-normal form for the doublet, though there it is not essential, as the frequencies of the two lines can themselves be taken as the two parameters. In all the work advantage is taken of the fact that the intervals between the lines are small compared with the frequencies; this simplifies the vibration theory a great deal. The great number of components in even a triplet makes it hard to see what course the search for a model ought to take; and I should say at once that I have not succeeded in finding any form that looks at all natural. There is too vast a field of possibilities to be certain that there is no such form, but it certainly does not offer itself readily (as it did for the doublet), and this fact, taken in conjunction with the failure of Voigt's model to agree with Landé's formula, I think rather suggests that the success of the doublet was accidental.

#### 4. *Force Factors and Emission Functions.*

We shall now develop certain general properties of vibrating systems. These belong to a well-established theory; but the case we are considering turns out simpler than the most general case—itself not very familiar—and so deserves treatment here. We shall work throughout with the Lagrangian form (denoting any such form by the symbol  $L$ ), as for the present problem nothing is gained by using the Hamiltonian.

We first examine the way in which the system reacts to the outside world. We intend to make use of the electromagnetic theory in the applications, but shall first discuss it with a greater generality, as the argument is simpler. Let the system have  $n$  coordinates  $q_1, q_2, \dots, q_n$ . Add a further one  $q_0$ , which on the one hand is used to set the system in motion, and on the other, to observe its motion. Then we have

$$L = \frac{1}{2} \sum_r \sum_s [a_{rs} \dot{q}_r \dot{q}_s - b_{rs} q_r q_s + 2c_{rs} \dot{q}_r q_s] \quad (r, s = 0, 1, 2 \dots n). \quad (4.1)$$

Without loss of generality,

$$a_{rr} = a_{rr}, \quad b_{rr} = b_{rr}, \quad c_{rs} = -c_{sr} \quad . \quad . \quad . \quad (4.2)$$

An equation of motion is then

$$\sum_{s=1}^n (a_{rs} \ddot{q}_s + 2c_{rs} \dot{q}_s + b_{rs} q_s) = -(a_{r0} \ddot{q}_0 + 2c_{r0} \dot{q}_0 + b_{r0} q_0). \quad (4.3)$$



If the system vibrates so that each coordinate is proportional to  $e^{ipt}$ , we define the expression on the right as  $Q_r$ , the external force on  $q_r$ , and have

$$Q_r = -q_0(b_{r0} + 2ipc_{r0} - p^2a_{r0}) \\ = e_r q_0. \quad \dots \dots \dots (4.4)$$

We call  $e_r$  the *force factor* for  $q_r$ . It is in general a function of  $p$  and is complex. Next consider emission. To observe this we study the motion of  $q_0$ . Its equation is

$$a_{00}\ddot{q}_0 + b_{00}\dot{q}_0 = -\sum_1^n (a_{0r}\ddot{q}_r + 2c_{0r}\dot{q}_r + b_{0r}q_r) \\ = -\sum_1^n (b_{0r} + 2ipc_{0r} - p^2a_{0r})q_r. \quad \dots (4.5)$$

Throughout the present paper we shall denote the complex quantity conjugate to any quantity  $z$  by the symbol  $\bar{z}$ . Then by virtue of (4.2)

$$a_{00}\ddot{q}_0 + b_{00}\dot{q}_0 = \sum_1^n \bar{e}_r q_r. \quad \dots \dots \dots (4.6)$$

The right-hand side represents the force which the system exerts on the test coordinate  $q_0$ , and so we can see the general form that emission must bear to absorption.

This is, of course, really one of the well-known reciprocal theorems of dynamics. Without going into details we can specialize it to deal with electromagnetic systems. We shall assume that the linkage is, in fact, solely dependent on the electric force, though more general cases could be as easily treated\*. Then to any coordinate  $x_r$ , which need not represent the position of an electron, there will correspond a force factor  $e_r$ , so that the force on the coordinate  $x_r$  will be  $e_r X$ . Our theorem tells us that the external action of the system will depend on an *emission function*  $\sum_1^n \bar{e}_r x_r$ . This is as much as we require for the present work. The most familiar case is, of course, that where  $e_r$  is the charge on an electron and so is purely real, and in this case  $\sum_1^n \bar{e}_r x_r$  is simply the electric moment; but the work gains symmetry by retaining the greater generality which obtains when  $x_r$  is not simply the position of an electron. The further details of emission, which we do not require, consist in constructing a Hertzian vector from the three components of the emission function and differentiating it to obtain the potentials and electric and magnetic forces.

\* For example, if a magneton reacted to the external magnetic force, it would be as easy to construct its effect in emission on the same principles.

5. *The Free Vibrations of the System.*

We next study the motions of the system, and shall introduce the condition which applies to multiplet lines, that all the vibrations have approximately equal frequencies—more precisely that the square of the difference between any two frequencies is negligible compared with the square of the frequencies themselves. This condition assimilates the problem rather closely to the familiar problem of vibrations about a position of equilibrium. The main difference lies in the fact that we have to deal with complex quantities and, speaking loosely, it will appear that half the symbols in the various formulæ must be replaced by their conjugates. We shall only outline the required theorems since the details can be filled in by analogy with the simpler theory.

We suppose that the kinetic energy is reduced to the sum of squares. Then the complete  $L$  is

$$\frac{1}{2} \sum_r (\dot{q}_r^2 - p_0^2 q_r^2) - \beta p_0 \sum_r \sum_s b_{rs} \dot{q}_r q_s + \omega \sum_r \sum_s c_{rs} \dot{q}_r q_s + F \sum_r e_r q_r. \quad (5.1)$$

Here  $\beta$  and  $\omega$  are two parameters of which the squares are negligible beside  $p_0$ ,  $F$  is a component of external force, and we can take

$$b_{sr} = b_{rs}, \quad c_{sr} = -c_{rs}. \quad (5.2)$$

We form the equations of motion

$$\ddot{q}_r + p_0^2 q_r + \sum_s (2\beta p_0 b_{rs} \dot{q}_s + 2\omega c_{rs} \dot{q}_s) = e_r F.$$

To solve we first equate the right-hand side to zero and put all coordinates proportional to  $e^{i(p_0 + \kappa)t}$ , so that  $p_0 + \kappa$  will be a frequency of emitted light. Approximating with  $\kappa$  small of the order of  $\beta$  and  $\omega$ , we have

$$-\kappa q_r + \sum_s (\beta b_{rs} + i\omega c_{rs}) \dot{q}_s = 0. \quad (5.3)$$

Put  $\beta b_{rs} + i\omega c_{rs} = h_{rs}$ . Then by virtue of (5.2),  $h_{sr} = \bar{h}_{rs}$ , and we require to discuss the solution of the system of equations

$$\sum_s h_{rs} \dot{q}_s = \kappa q_r.$$

This depends on the determinantal equation

$$\begin{vmatrix} h_{11} - \kappa & h_{12} & \dots & h_{1n} \\ h_{21} & h_{22} - \kappa & \dots & h_{2n} \\ \dots & \dots & \dots & \dots \\ h_{n1} & h_{n2} & \dots & h_{nn} - \kappa \end{vmatrix} = 0, \quad (5.4)$$

which we shall call the period equation.

In almost the same way as is used when the  $h$ 's are real, it can be shown that this equation has only real roots\*, and the same conditions hold as to the vanishing of first minors for double roots, etc. We may at once observe also that the equation only involves  $\omega^2$ ; so when  $\omega$  is small compared with  $\beta$ , the roots will be placed symmetrically about their values for  $\omega=0$ —a feature of the anomalous Zeeman effect.

Associated with each root we can determine a set of ratios for the  $q$ 's; for  $\kappa=\kappa_a$  we have  $q_r=l_{ra}u_a$ . The normal coefficients  $l_{ra}$  satisfy the conditions

$$\kappa_a l_{ra} = \sum_s l_{sa} h_{rs}. \quad . \quad . \quad . \quad (5.5)$$

We can easily establish a set of quasi-orthogonal conditions between the normal coefficients. Thus if  $\kappa_a, \kappa_\beta$  are two distinct solutions of (5.4), we have

$$\sum_r l_{ra} \tilde{l}_{r\beta} = 0. \quad . \quad . \quad . \quad (5.6)$$

As only the ratios of the  $l$ 's have so far been defined, we may fix their magnitudes by the normalizing conditions

$$\sum_r l_{ra} \tilde{l}_{ra} = 1. \quad . \quad . \quad . \quad (5.7)$$

When there is a double root the ratios  $l_{ra}$  are not completely determinate, but just as in the ordinary case we can always find a pair of sets of values which satisfy the orthogonal condition together. So, too, for higher degrees of multiplicity, and no trouble arises on this account. It is important to note this point because there are always multiple roots in strong magnetic fields.

When the complete system of normal coefficients has been found, we can make the substitution

$$q_r = \sum_a l_{ra} u_a. \quad . \quad . \quad . \quad (5.8)$$

By using (5.6) and (5.7) we can find the inverse equations, which take a form slightly different from that of the ordinary theory of vibrations about equilibrium.

$$u_a = \sum_r \tilde{l}_{ra} q_r. \quad . \quad . \quad . \quad (5.9)$$

We can then establish the inverted forms of the orthogonal and normalizing conditions.

$$\left. \begin{aligned} \sum_a l_{ra} \tilde{l}_{sa} &= 0 & \text{if } r \neq s \\ &= 1 & \text{if } r = s \end{aligned} \right\}, \quad . \quad . \quad . \quad (5.10)$$

and can thence prove that

$$h_{rs} = \sum_a \kappa_a l_{ra} \tilde{l}_{sa}. \quad . \quad . \quad . \quad (5.11)$$

\* See, for instance, Whittaker, 'Analytic Dynamics,' p. 179.

We must also consider the behaviour of the force factors. We define

$$e_a = \sum_r e_r \tilde{l}_{ra}, \quad . \quad . \quad . \quad (5.12)$$

then inverting

$$e_r = \sum_a e_a \tilde{l}_{ra} \quad . \quad . \quad . \quad (5.13)$$

The emission function is transformed

$$\sum_r \tilde{e}_r q_r = \sum_a \tilde{e}_a u_a \quad . \quad . \quad . \quad (5.14)$$

When there are equal roots, the  $\tilde{l}$ 's are partly arbitrary. It is always possible, and often convenient, to select them in such a way that all but one of the associated force factors shall vanish.

### 6. The Multiplet without Magnetic Field.

We shall now consider the model for a multiplet without magnetic field. The system is to have all its frequencies nearly equal and their spacing is to depend on a single parameter. It would not be natural for this parameter to occur in different parts of  $L$ , and we shall therefore take it that the potential energy alone is not in the form of a sum of squares. The results would be much the same if we modified the kinetic energy instead. The atom can only be isotropic if the terms in  $L$  involving the directions  $x, y, z$  are all separated, and it will suffice to consider one of them alone. For the  $x$ -direction, we have

$$L = \frac{1}{2} \sum_r (\dot{x}_r^2 - p_0^2 x_r^2) - \beta p_0 \sum_r \sum_s b_{rs} x_r x_s + X \sum_r e_r x_r. \quad (6.1)$$

Here  $X$  is the external electric force in the  $x$ -direction and  $\beta$  is small. The equations of motion are

$$\ddot{x}_r + p_0^2 x_r + 2\beta p_0 \sum_s b_{rs} x_s = e_r X. \quad . \quad . \quad (6.2)$$

We can solve for the natural frequencies as in (5.4) and with the help of the solution can transform (6.2) to

$$\ddot{u}_a + (p_0^2 + 2p_0 \kappa_a) u_a = e_a X. \quad . \quad . \quad (6.3)$$

Under a force  $X$  proportional to  $e^{i\nu t}$  the emission function then is

$$\sum_r \tilde{e}_r v_r = \sum_a \tilde{e}_a u_a = X \sum_a \frac{e_a \tilde{e}_a}{(p_0 + \kappa_a)^2 - \nu^2}, \quad . \quad . \quad (6.4)$$

and from this the refractive index can be deduced by well-known principles.

In order to discuss absorption we have to introduce damping terms into the equations. The model is illuminated by a wave of the form  $X = \int_0^\infty \phi(p) e^{i\nu t} dp$ . If the damping factors are small, it is not hard to show that the response of

the model to such a force is independent of their magnitudes; in fact, that

$$u_a = -\frac{i\pi}{2} e_a \frac{\phi(p_0 + \kappa_a)}{p_0 + \kappa_a} e^{i(p_0 + \kappa_a)t}.$$

Absorption is observed by measuring the extinction of light, initially distributed uniformly over the spectrum, as it passes through the substance. This extinction is produced by the interference between the incident light and the scattered light from the atoms. Whatever may be the mechanism of absorption inside the atoms, the external reaction must still depend on the emission function and so must give a factor  $e_a \tilde{e}_a$  for the line of frequency  $p_0 + \kappa_a$ . The other factors are approximately constant. Thus absorption is determined from dispersion, and though we have to postulate some damping its character is without effect on the result; it only affects the breadths of the lines, a matter we are not going to discuss.

To find the emission we take arbitrary conditions of projection, so that the initial value of  $x_r$  is  $x_r^0$  (for simplicity we omit initial velocities). Corresponding to these we can determine  $u_a^0$ , etc. by (5.9). The emission function then becomes

$$\sum_a \tilde{e}_a u_a^0 e^{i(p_0 + \kappa_a)t},$$

and if none of the roots  $\kappa_a$  are equal, the intensity corresponding to the frequency  $p_0 + \kappa_a$  is proportional to

$$|\tilde{e}_a u_a^0|^2. \quad \dots \dots \dots (6.5)$$

Now, if we have equipartition among the values  $x_r^0$ , we shall also have it for the  $u_a^0$ 's. The average value of  $|u_a^0|^2$  is then the same for all  $a$ , and hence the intensity of the line is proportional to  $e_a \tilde{e}_a$ . A slightly extended argument would have allowed for initial velocities. When the system contains equal roots—say  $\kappa_a, \kappa_\beta$ , we should get an intensity  $|\tilde{e}_a u_a^0 + \tilde{e}_\beta u_\beta^0|^2$ . This need not cause any trouble, for the choice of the normal modes is here partly undetermined, and they may be chosen so that  $e_\beta = 0$ , and then the intensity reduces to its simpler form. We have discussed the intensities of emission and absorption for convenience without magnetic field. It is easy to see that with a few trivial changes the arguments will apply just as well when the equations of motion contain gyroscopic terms.

It is natural to choose  $p_0$  as the centre of gravity of the multiplet. This implies a condition between the  $b$ 's which we shall now work out. The centre of gravity is at  $p_0$  if

$$\sum_a \kappa_a e_a \tilde{e}_a = 0.$$

Now, by (5.12), (5.11) (here simplified because all the quantities are real)

$$\begin{aligned}\sum_a \kappa_a e_a \tilde{e}_a &= \sum_a \sum_s \sum_r \kappa_a e_s \tilde{l}_{sa} \tilde{e}_r l_{ra} \\ &= \sum_r \sum_s b_{rs} e_s \tilde{e}_r = 0, \quad . \quad . \quad . \quad (6.6)\end{aligned}$$

which is the required condition.

To illustrate the whole process we may take the following example :

$$L = \frac{1}{2} \sum_1^3 (\dot{x}_r^2 - p_0^2 x_r^2) + 2\beta p_0 (x_1 x_2 + x_2 x_3 + x_3 x_1) + X e x_1. \quad (6.7)$$

The period equation is

$$\begin{vmatrix} \kappa, & \beta, & \beta \\ \beta, & \kappa, & \beta \\ \beta, & \beta, & \kappa \end{vmatrix} \equiv (\kappa - \beta)^2 (\kappa + 2\beta) = 0.$$

The following scheme gives the normal coefficients, etc. :

	$u_1$	$u_2$	$u_3$
$x_1$	$\sqrt{2/3}$	0	$1/\sqrt{3}$
$x_2$	$-1/\sqrt{6}$	$1/\sqrt{2}$	$1/\sqrt{3}$
$x_3$	$-1/\sqrt{6}$	$-1/\sqrt{2}$	$1/\sqrt{3}$
$\kappa_a$	$\beta$	$\beta$	$-2\beta$
$e_a/e$	$\sqrt{2/3}$	0	$1/\sqrt{3}$

} . . . (6.8)

There are thus two lines respectively at  $p_0 + \beta$  and  $p_0 - 2\beta$ , and the first has double the intensity of the second. In fact they are the D lines. Moreover, to conform with Minakowski's experiments  $e$  is to be given the value corresponding to that of an ordinary electron.

The form of  $L$  suggests that it might be given a more physical meaning by modifying the kinetic instead of the potential energy. In this case the complete formula for  $L$  would contain terms

$$(2\beta/p_0)(\dot{x}_1 \dot{x}_2 + \dot{y}_1 \dot{y}_2 + \dot{z}_1 \dot{z}_2 + \dot{x}_1 \dot{x}_3 + \dots), \quad (6.9)$$

which are suggestive of electromagnetic induction. In the absence of other similar cases it is not possible to evolve this idea further.

We may here refer to an important difficulty which occurs in the designing of models. It applies to cases both with and without magnetic fields. All that is ever observed is the emission function, and it is possible for a system to have natural frequencies which never exhibit themselves. All

that is necessary for this is that the associated  $e_a$  should vanish. We shall refer to a mode of vibration having this property as *blind*, and in general the same term will be applied to any degree of freedom which has zero force factor—for example, our model for the D lines has one active and two blind electrons. The possible existence of blind vibrations makes great trouble in designing models, for their introduction often simplifies the formulæ (as an example will show below), and this compels one to try a great many more systems than would otherwise be necessary.

### 7. *The General Model for the Zeeman Effect.*

In the presence of a magnetic field the system is no longer isotropic, but if the field is along  $z$  there will persist a circular symmetry for  $x$  and  $y$ . As witnessed by magnetic double refraction the anisotropy is proportional to the field. We therefore construct the model by adding on gyroscopic terms; we shall take these directly proportional to the magnetic field, and shall suppose the force factors unaltered. These are the simplest assumptions we can make; we shall see later that they cannot apply to all multiplets, but nevertheless a good deal of the work can be easily adapted to such cases.

The condition of circular symmetry requires that  $L$  shall be unchanged when  $y$  is written for  $x$  and  $-x$  for  $y$ , and this implies that there can be no terms in  $xz$  and  $yz$ . Consequently the terms in  $x$  and  $y$  can be separated off, and we can discuss the model for the  $\perp$  components apart from the  $\parallel$ . As the Zeeman effect is usually described by reference to the undisplaced lines, the study of special models goes most conveniently in terms of the semi-normal form, but there is no gain in principle, so that we shall retain the generality.

We start with the most general form of  $L$  which satisfies the condition of circular symmetry.

$$L = \frac{1}{2} \sum_r (\dot{x}_r^2 + \dot{y}_r^2 - p_0^2 x_r^2 - p_0^2 y_r^2) - \beta p_0 \sum_r \sum_s b_{rs} (x_r \dot{x}_s + y_r \dot{y}_s) \left. \begin{aligned} &+ \omega \sum_r (x_r \dot{y}_r - \dot{x}_r y_r) + \omega \sum_r \sum_s [f_{rs} (\dot{x}_r x_s + \dot{y}_r y_s) \\ &+ g_{rs} (x_r \dot{y}_s - \dot{x}_s y_r)] + X \sum_r e_r \dot{x}_r + Y \sum_r e_r \dot{y}_r. \end{aligned} \right\} \quad (7.1)$$

Here  $f, g$  are constants, and

$$f_{sr} = -f_{rs}, \quad g_{sr} = g_{rs}; \quad \dots \quad (7.2)$$

$\omega$  stands for the Larmor rotation  $eH/2mc$ , where  $H$  is

the field, and it has been convenient to separate out a set of terms corresponding to the normal Zeeman effect.

A pair of equations is :

$$\left. \begin{aligned} \ddot{x}_r + p_0^2 x_r + 2\beta p_0 \Sigma_s b_{rs} x_s - 2\omega \dot{y}_r + 2\omega \Sigma_s (f_{rs} \dot{x}_s - g_{rs} \dot{y}_s) &= e_r X. \\ \ddot{y}_r + p_0^2 y_r + 2\beta p_0 \Sigma_s b_{rs} y_s + 2\omega \dot{x}_r + 2\omega \Sigma_s (f_{rs} \dot{y}_s + g_{rs} \dot{x}_s) &= e_r Y. \end{aligned} \right\} \quad (7.3)$$

The solution can be simplified by Voigt's artifice of putting

$$\zeta_r = x_r + iy_r, \quad Z = X + iY. \quad (7.4)$$

Then we have

$$\ddot{\zeta}_r + p_0^2 \zeta_r + 2\beta p_0 \Sigma_s b_{rs} \zeta_s + 2\omega [i\dot{\zeta}_r + \Sigma_s (f_{rs} + ig_{rs}) \dot{\zeta}_s] = e_r Z, \quad (7.5)$$

and a similar equation in  $\bar{\zeta}_r$  and  $\bar{Z}$ . To find the free vibrations we omit the right-hand side and put all co-ordinates proportional to  $e^{ipt}$ . Making a slight change in the notation, we take

$$p = p_0 - \omega + \kappa. \quad (7.6)$$

In this way we have separated the right- and left-handed components and have referred each to the position it would have if the Zeeman effect were normal.

Write  $h_{rs} = if_{rs} - g_{rs}$ , then by (7.2)  $h_{rr} = \bar{h}_{rr}$ . (7.7)

We omit the distinction between  $p$  and  $p_0$  in the small terms and the equation becomes

$$-\kappa \zeta_r + \Sigma_s (\beta b_{rs} + \omega h_{rs}) \zeta_s = 0, \quad (7.8)$$

and this is of the type of (5.3). In forming the corresponding equation for  $\bar{\zeta}_r$  it is necessary to change the sign of  $\omega$  and to take the conjugates of all the complex quantities.

The period equation is

$$\left| \begin{array}{ccc} \beta b_{11} + \omega h_{11} - \kappa, & \beta b_{12} + \omega h_{12}, & \dots \\ \beta b_{21} + \omega h_{21}, & \beta b_{22} + \omega h_{22} - \kappa, & \dots \\ \dots & \dots & \dots \end{array} \right| = 0, \quad (7.9)$$

and according to the relative magnitudes of  $\beta$  and  $\omega$  we have the anomalous Zeeman effect and the Paschen-Back effect. We shall refer to these simply as the *weak* and *strong effects* respectively. To deal with the weak effect we refer the system to its vibrations without field, that is we suppose  $L$  reduced to its semi-normal form, and this is given if we take  $b_{rs} = 0$  for  $r \neq s$ . The period equation will then separate into groups for each of which  $b_{rr}$ 's have the same value. For example, if one member of the multiplet shows a



Zeeman effect with two components, we must have  $b_{11}=b_{22}$ , and can then separate out from (7.9) an equation

$$\begin{vmatrix} \beta b_{11} + \omega h_{11} - \kappa, & \omega h_{12} \\ \omega h_{21}, & \beta b_{11} + \omega h_{22} - \kappa \end{vmatrix} = 0. \quad (7.10)$$

The known positions of the components then give us two relations between  $h_{11}$ ,  $h_{12}$ ,  $h_{21}$ ,  $h_{22}$ .

Now consider the strong effect, where all multiplets give the normal Zeeman effect. To examine it we simply omit the terms in  $\beta$ . Now it is obviously not possible for all the roots of (7.9) to vanish, for this would imply a normal effect also in weak fields; but this is not needed, it is enough if all solutions are blind for which  $\kappa \neq 0$ . The necessary and sufficient condition for the strong effect is thus that for any  $\kappa_a$  differing from zero the emission function should vanish, that is,  $\sum_r e_r l_{ra} = 0$ . This implies that the set of quantities  $e_r$  are orthogonal to the normal coefficients  $l_{ra}$  which belong to every non-zero root  $\kappa_a$ . Hence, as the  $e_r$ 's cannot all vanish, they must be a set of normal coefficients for one of the modes orthogonal to all these, that is, for some mode for which  $\kappa = 0$ . Substituting in (5.5) we thus get

$$\sum_s e_s h_{rs} = 0, \quad . \quad . \quad . \quad . \quad . \quad (7.11)$$

and as it is easy to see that these conditions imply that at least one root of the period equation must vanish, they constitute a set of necessary and sufficient conditions for the strong effect.

In one particular case the strong condition can be given an even simpler form. Suppose, as in the example of the last section, that only one electron is active and all the rest are blind. Then we have  $e_r = 0$  except for  $e_1$ . The conditions for the strong effect then are simply that  $h_{r1} = 0$  for all  $r$ .

By the general argument of § 5 the  $\Pi$  components will be symmetrical about the undisplaced lines in weak fields. It will only involve  $z$ 's, and there will be a set of gyroscopic terms with coefficients proportional to  $\omega$ . We take  $\kappa = p_0 - p$  in this case and the argument goes much as before; the only distinction is that the system of equations does not split into two, and that the  $h$ 's are purely imaginary. The condition for the strong effect is exactly as before.

### 8. *The Magnetic Gyration of Light.*

The assumed form of model implies an interesting theorem concerning the Faraday effect. However weak the field, light of wave-length distant from the multiplet will show no

trace of the anomalous effect, but will be rotated to an extent exactly given by the normal Zeeman effect. There is a crude way of explaining magnetic gyration which leads to a wrong result. The argument is as follows. Draw a complete dispersion curve for the undisplaced line, and copy it twice displaced respectively to the right and left. As one wave corresponds to right-handed polarized light and the other to left-handed, the difference between the two curves should give the net rotatory effect. If the line splits into more than a single pair of components we should expect that an appropriate averaging of their influences would give the right result. This argument would suggest for the rotation of sodium an amount equal to

$$(1 \times \frac{5}{3} + 3 \times 1 + 2 \times \frac{4}{3}) / (1 + 3 + 2) = 11/9$$

of the normal rotation. The fallacy lies in the assumption that the dispersion curves may be shifted unchanged in form. This is only approximately true; the comparative importance of the various lines changes only slightly with the field, but as the gyration is itself a differential effect, these small changes become sensible.

Let the amplitude of the incident light be proportional to  $e^{i\omega t}$ , and now suppose that  $p$  is not at all near to  $p_0$ . The equations of motion are

$$\zeta_r(p_0^2 - p^2 - 2\omega p) + 2\beta p_0 \Sigma_s h_{rs} \zeta_s + 2\omega p \Sigma_s h_{rs} \zeta_s = e_r Z. \quad (8.1)$$

The first term is now large, and we can solve by approximation and have

$$\zeta_r = Z \left\{ \frac{e_r}{p_0^2 - p^2} - 2\beta p_0 \Sigma_s \frac{b_{rs} e_s}{(p_0^2 - p^2)^2} + 2\omega p \frac{e_r}{(p_0^2 - p^2)^2} - 2\omega p \Sigma_s \frac{h_{rs} e_s}{(p_0^2 - p^2)^2} \right\}. \quad (8.2)$$

Then the emission function is

$$\Sigma_r \tilde{e}_r \zeta_r = Z \left\{ \Sigma_r \frac{e_r \tilde{e}_r}{p_0^2 - p^2} - 2\beta p_0 \Sigma_r \Sigma_s \frac{b_{rs} e_s \tilde{e}_r}{(p_0^2 - p^2)^2} + 2\omega p \Sigma \frac{e_r \tilde{e}_r}{(p_0^2 - p^2)^2} - 2\omega p \Sigma_r \Sigma_s \frac{h_{rs} e_s \tilde{e}_r}{(p_0^2 - p^2)^2} \right\}. \quad (8.3)$$

By (6.6) the second term will vanish if  $p_0$  has been chosen as the centre of gravity of the multiplet. The fourth vanishes by virtue of (7.11), the conditions for the strong effect. Consequently

$$\Sigma_r \tilde{e}_r \zeta_r = Z \Sigma_r \frac{e_r \tilde{e}_r}{p_0^2 - p^2} \left( 1 + \frac{2\omega p}{p_0^2 - p^2} \right), \quad (8.4)$$

which is exactly the result that would be obtained if there

were no anomalous Zeeman effect at all. So we conclude that light at any considerable distance from the multiplet will be gyrate according to the normal Lorentz principle, no matter how weak the magnetic field. When the incident light has frequency near that of the multiplet of course this does not hold, since the approximate method of solution fails; here the actual anomalies of the Zeeman effect will show themselves. In intermediate cases formulæ can be found by regarding  $\omega$ , but no longer  $\beta$ , as small compared to  $p - p_0$ . The validity of Voigt's type of model could evidently be partially tested by experiments which verified whether the dispersion becomes normal at great distances from the multiplet.

There is a well-known formula, due to Becquerel\*, whereby the value of  $e/m$  for any substance can be deduced from measures of its gyration and dispersion, and these measures need not be carried out near its regions of absorption. The formula is

$$R = \frac{e}{2mc^2} \lambda \frac{dn}{d\lambda}, \quad . \quad . \quad . \quad . \quad . \quad (8.5)$$

where

$n$  is the refractive index,  
 $\lambda$  is the wave-length,  
 $R$  is the "Verdet constant,"  
 and  $e$  is measured in E.S.U.

This has been applied to a good many substances, and with one exception the values found are well below the normal value. The anomalous Zeeman effect always involves increased values of  $e/m$ , and our theorem shows that we need not expect these to be reproduced in Becquerel's formula. There remains the difficulty of the values being too low. The infra-red bands of a substance depend on nuclear motions and so should lower the value, but they play quite an insignificant part in the refraction of blue and ultra-violet light. We should thus expect that if  $e/m$  is calculated from (8.5) for different wave-lengths, the values will be low in the infra-red and increase towards a limit in the ultra-violet. The following figures show this for the case of water, which has a band in the near infra-red.

Wave-length in $\mu$ .....	1.000	.900	.800	.701	.589	.518	.437	.361	.275	.250
$\frac{e/m}{(e/m)_{\text{norm.}}} \times 100$ }	26	33.6	47.5	59.6	68.0	74.2	77.4	78.3	78.6	78.7

More striking is the case of the permanent gases, since they

\* Becquerel, *C. R.* vol. cxxv. p. 679 (1897).

have no infra-red absorption. Thus hydrogen gives a value within 1 per cent. of the normal for all wave-lengths not very near to the point in the far ultra-violet where it ceases to be transparent—this is the only substance known that is normal; whereas nitrogen gives 69 per cent. normal over the same range of wave-lengths. The fact that it is hydrogen that is normal shows that the abnormality cannot be due to nuclear motions, for these would certainly be larger in hydrogen than in anything else. On the lines of the present section we can only get the observed result by supposing that the absorption bands in the ultra-violet show an anomalous Paschen-Back effect! An alternative and more probable explanation will be given in the next section.

### 9. *The Failure of the Model for some Lines.*

Consideration of a certain type of multiplets shows that the model with which we have been working cannot always be adequate. Take the line 2537 of mercury. This is the only surviving member of a triplet  $1S-2p$ . In a magnetic field it gives a single pair of  $\pm$  components, but with a separation  $3/2$  of the normal. This could, of course, be easily represented mechanically, but would of necessity imply the same abnormality in strong fields. In order to represent the strong effect we must bring in the other lines of the triplet somehow. Now a triplet would only show two lines if the force factor associated with the third happened to vanish in the absence of the field. In this case it would be observed that the absent line began to make its appearance with an intensity proportional to the square of the magnetic force, and the strong effect could finally appear in the normal way. Unfortunately this explanation will not do if only one line of the triplet is ordinarily present. For let us suppose that the model is reduced to semi-normal form, and that it is the line 1 that is active. All the force factors except  $e_1$  vanish, even if 1 is a multiple root. The condition for the strong effect is then that  $h_{r1}=0$  and in particular that  $h_{11}=0$ , and so there can be no anomalous weak effect.

The only way of overcoming this difficulty seems to be to alter our assumptions and to suppose that the  $h$ 's and  $e$ 's are themselves functions of the magnetic field. The conditions for the strong effect will take exactly the same form as before, but owing to the variability of the parameters will not be nearly so significant. In the strong field (7.11) will still be true, but we shall not be able to apply it to (8.3),

because the  $e$ 's and  $h$ 's will there have different values. The transition from the weak to the strong effect in mercury can be made to occur either by varying the  $e$ 's or the  $h$ 's; it should be accompanied by the appearance of the other lines of the triplet with intensities proportional to the square of the field. When the field is weak we need no longer have  $\Sigma e_i h_{rs} = 0$ , and so there is no longer any necessity that Becquerel's formula should lead to the normal  $e/m$ .

A piece of evidence in favour of making the  $h$ 's vary is provided by the theory of Landé referred to in § 3. This suggests that Voigt's values of the Zeeman effect for intermediate fields are wrong, and the only way of altering them is to allow the  $h$ 's to change. The conditions for the strong effect are not at all stringent and can be satisfied by a very wide choice of  $e$ 's and  $h$ 's.

The importance of this part of our work lies in the fact that gyration gives information about the beginnings of the transition from the weak to the strong effect. It does not show how the positions of the components change, but partially reveals the change in their relative intensities to a higher order than is directly observable. The quantum theory has successfully explained the intensities in weak fields, and the suggested information should act as a help to its further development. The experiment has the advantage of only depending on refinements in optics, whereas most methods of attack would seem to involve the production of magnetic fields of such great strength as must always be unattainable.

#### 10. *The D Lines, $\perp$ Component.*

With the use of the principles of §§ 5-7 we shall now discuss the complete model for the doublet. For the  $\perp$  components Sommerfeld gives the equations

$$\left. \begin{aligned} \ddot{\xi}_1 + 2i\omega\dot{\xi}_1 + p_1^2\xi_1 + \frac{2}{3}i\omega(\dot{\xi}_1 + \epsilon\dot{\xi}_2 + \epsilon^2\dot{\xi}_3) &= eZ, \\ \ddot{\xi}_2 + 2i\omega\dot{\xi}_2 + p_2^2\xi_2 + \frac{2}{3}i\omega(\dot{\xi}_2 + \epsilon\dot{\xi}_3 + \epsilon^2\dot{\xi}_1) &= eZ, \\ \ddot{\xi}_3 + 2i\omega\dot{\xi}_3 + p_2^2\xi_3 + \frac{2}{3}i\omega(\dot{\xi}_3 + \epsilon\dot{\xi}_1 + \epsilon^2\dot{\xi}_2) &= eZ, \end{aligned} \right\} \quad (10.1)$$

where  $p_1, p_2$  are the frequencies of  $D_1$  and  $D_2$  and  $\epsilon$  is a cube root of unity. These equations, of course, represent a mechanical system, but if we put down the Lagrangian from which they are derived it will be found to contain a very

large number of terms, some of which involve the irrationality  $\sqrt{3}$  arising from  $e$ . In fact, in spite of the symmetry, the model is not really simple. Another point in which it cannot be supposed to be very near to reality is that it requires three similar electrons, and the quantum theory leads us to expect that in sodium one electron is more important than all the others. This matter was discussed in § 3 and need not be further dealt with here.

We have shown how the doublet can be simplified by departing from the semi-normal form, when there is no field. If we take that idea and transform Voigt's equations by means of it we arrive (by rather heavy algebra involving the special choice of one parameter) at a new form from which all irrationalities have disappeared. As we are going to discuss the making of models later, we shall simply here give the result. Take

$$L = \frac{1}{2} \Sigma_1^3 (\dot{x}_r^2 + \dot{y}_r^2) - \frac{1}{2} p_0^2 \Sigma_1^3 (x_{r1}^2 + y_r^2) \\ + 2\beta p_0 (x_1 x_2 + y_1 y_2 + x_2 x_3 + y_2 y_3 + x_1 x_3 + y_1 y_3) \\ + \omega (x_1 \dot{y}_1 - \dot{x}_1 y_1) + \frac{1}{2} \omega (x_2 \dot{y}_2 - \dot{x}_2 y_2 + x_3 \dot{y}_3 - \dot{x}_3 y_3) \\ + \frac{1}{2} \omega (x_2 \dot{x}_3 - \dot{x}_2 x_3 + y_3 \dot{y}_3 - \dot{y}_2 y_3) + e (X x_1 + Y y_1) \quad (10.2)$$

The equations of motion in  $x$  and  $y$  can be combined into equations in  $\xi$  as in § 7. These are

$$\left. \begin{aligned} \ddot{\xi}_1 + p_0^2 \xi_1 - 2\beta p_0 (\xi_2 + \xi_3) + 2i\omega \dot{\xi}_1 &= eZ, \\ \ddot{\xi}_2 + p_0^2 \xi_2 - 2\beta p_0 (\xi_3 + \xi_1) + 3i\omega \dot{\xi}_2 - \omega \dot{\xi}_3 &= 0, \\ \ddot{\xi}_3 + p_0^2 \xi_3 - 2\beta p_0 (\xi_1 + \xi_2) + 3i\omega \dot{\xi}_3 + \omega \dot{\xi}_2 &= 0. \end{aligned} \right\} \quad (10.3)$$

The strong effect is verified at once because the coefficient of  $\dot{\xi}_1$  is simply  $2i\omega$ . We shall not examine the complete solution for all strengths of field, because the equations are only transformations of those of Voigt, and so must give exactly the same frequencies and intensities. But as illustrating the type of solution we shall give the weak effect. The period equation is (with  $p = p_0 - \omega + \kappa$ )

$$\begin{vmatrix} \kappa & \beta & \beta \\ \beta & \kappa + \frac{\omega}{2} & \beta + \frac{i\omega}{2} \\ \beta & \beta - \frac{i\omega}{2} & \kappa + \frac{\omega}{2} \end{vmatrix} \equiv (\kappa - \beta)[(\kappa + \omega)(\kappa + \beta) - 2\beta^2] = 0. \quad (10.4)$$

The approximate solutions are  $\kappa = \beta$ ,  $\beta - \frac{2}{3}\omega$ ,  $-2\beta - \frac{1}{3}\omega$ , and the complete determination of the frequencies and normal coefficients is given in the following scheme:—

	$u_1$	$u_2$	$u_3$
$\zeta_1$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
$\zeta_2$	$\frac{-1+i}{2\sqrt{2}}$	$\frac{-1-3i}{2\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
$\zeta_3$	$\frac{-1-i}{2\sqrt{2}}$	$\frac{-1+3i}{2\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
$p-p_0$	$\beta - \omega$	$\beta - \frac{5}{3}\omega$	$-2\beta - \frac{4}{3}\omega$
$e_a/e$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$

} . . (10.5)

It must be remembered that this is to be read horizontally, thus

$$\zeta_2 = \frac{-1+i}{2\sqrt{2}} u_1 + \frac{-1-3i}{2\sqrt{6}} u_2 + \frac{1}{\sqrt{3}} u_3.$$

If it is wished to read it vertically the conjugates must be taken, thus:

$$u_1 = \frac{1}{\sqrt{2}} \zeta_1 + \frac{-1-i}{2\sqrt{2}} \zeta_2 + \frac{-1+i}{2\sqrt{2}} \zeta_3.$$

From the force factors we at once derive that the intensities of the lines are as  $\frac{1}{2} : \frac{1}{4} : \frac{1}{8}$  or 3:1:2, as is confirmed by experiment. This is subject to the assumption of equipartition between the coordinates, and if we imagined special forms of excitation, we could obtain other results. For example, suppose that the second electron was alone excited. From (6.5) we should then have intensities in the ratios  $(\frac{1}{4} \cdot \frac{1}{2}) : (\frac{1}{24} \cdot \frac{1}{6}) : (\frac{1}{3} \cdot \frac{1}{3})$  or 18:10:16. If only the first were excited they would be 9:1:4. Resonance radiation must be supposed to arise from action on the first electron, and the erroneous values for the intensities are a further proof of the necessity for some sort of reorganization between the processes of absorption and re-emission.

## 11. The D Lines, II Component.

Voigt's model for the II components is a little more artificial, for he introduces two frequencies which are blind at all strengths of the field. By this means he splits the equations of motion into half in the same way as can always be done for the I components. His equations are

$$\left. \begin{aligned} \ddot{\xi}_1 + 2i\omega\dot{\xi}_1 + p_1^2\xi_1 - \frac{2}{3}i\omega(\dot{\xi}_1 + \dot{\xi}_2 + \dot{\xi}_3) &= eZ', \\ \ddot{\xi}_2 + 2i\omega\dot{\xi}_2 + p_2^2\xi_2 - \frac{2}{3}i\omega(\dot{\xi}_1 + \dot{\xi}_2 + \dot{\xi}_3) &= eZ', \\ \ddot{\xi}_3 + 2i\omega\dot{\xi}_3 + p_3^2\xi_3 - \frac{2}{3}i\omega(\dot{\xi}_1 + \dot{\xi}_2 + \dot{\xi}_3) &= eZ', \end{aligned} \right\} \quad (11.1)$$

where  $\zeta = z + i\omega$ ,  $Z' = Z(1 + i)$ .

The extra coordinates  $w$  make the completed system anisotropic unless the force factors are chosen to be  $1/\sqrt{2}$  of the corresponding ones for the I coordinates. If we apply the transformation quoted in the last section to these equations, we obtain

$$\left. \begin{aligned} L = \frac{1}{2}\Sigma_1^2 [(\dot{z}_r^2 + \dot{w}_r^2) - p_0^2(z_r^2 + w_r^2)] \\ + 2\beta p_0(z_1z_2 + z_2z_3 + z_3z_1 + w_1w_2 + w_2w_3 + w_3w_1) \\ + \omega(z_2\dot{w}_2 - \dot{z}_2w_2 + z_3\dot{w}_3 - \dot{z}_3w_3) + Zez_1. \end{aligned} \right\} \quad (11.2)$$

We have made a small further change in that  $Z$  is the actual electric force, so that  $w_1$  is blind, and we have avoided the necessity of having a force factor different from those of  $x_1$  and  $y_1$ . The strong condition is satisfied by the absence of terms in  $\omega$  involving  $z_1$ .

As before, we shall only give the effects in weak fields; in stronger fields they go exactly as in Sommerfeld's paper\*. We follow him in splitting the equations into two by the substitution  $\zeta = z + i\omega$  and have equations

$$\left. \begin{aligned} \ddot{\xi}_1 + p_0^2\xi_1 - 2\beta p_0(\xi_2 + \xi_3) &= eZ, \\ \ddot{\xi}_2 + p_0^2\xi_2 - 2\beta p_0(\xi_1 + \xi_3) + 2i\omega\dot{\xi}_2 &= 0, \\ \ddot{\xi}_3 + p_0^2\xi_3 - 2\beta p_0(\xi_1 + \xi_2) + 2i\omega\dot{\xi}_3 &= 0. \end{aligned} \right\} \quad (11.3)$$

Taking  $p = p_0 + \kappa$ , the period equation is

$$\left| \begin{array}{ccc} \kappa, & \beta, & 1 \\ \beta, & \kappa + \omega, & \beta \\ \beta, & \beta, & \kappa + \omega \end{array} \right| \equiv (\kappa - \beta + \omega)[(\kappa - \beta)(\kappa + 2\beta) + \kappa\omega] = 0, \quad (11.4)$$

\* Sommerfeld, *loc. cit.*



and the normal coefficients are given by the scheme

	$u_1$	$u_2$	$u_3$
$z_1$	0	$\frac{2}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
$z_2$	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
$z_3$	$-\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
$p-p_0$	$\beta-\omega$	$\beta-\frac{1}{3}\omega$	$-2\beta-\frac{2}{3}\omega$
$e_a/e$	0	$\frac{2}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$

. . (11.5)

The intensities are in the ratio 0 : 2 : 1.

Before leaving the subject of models for doublets, we may note that in both **I** and **II** components the coordinates  $x_1, y_1, z_1$  alone have force factors, so that we may, so to speak, regard the rest as having no sense of direction. This suggests that the blind coordinates called  $x_2$  etc. might really be in some quite other direction, and if they were we could in some ways give the formulæ more natural interpretations. Thus we might regard the coefficient of  $\omega$  in (11.2) as due to the fact that  $z_2, z_3$  were really in the direction  $x$ , and  $w_2, w_3$  in the direction  $y$ , and then we could interpret these terms as a normal effect of the magnetic field. The main difficulty is that, in proportion as we give these terms simple meanings, the terms in the potential energy become complicated. Without some model for another type of multiplet to guide us we cannot see which of several forms is the most natural, and so shall leave our model as it stands.

## 12. *The Construction of Models.*

We now consider what general principles ought to guide us in designing models for other types of multiplet. These have, of course, to conform to specified conditions as to frequencies and intensities. This means that we are given a set of  $u$ 's and their force factors, and our object is to discover a linear transformation which will reduce them to equations derived from some simple Lagrangian function. We are to preserve the condition that the kinetic energy remains a sum

of squares, and so the permissible transformations are any set of mutually orthogonal coefficients. Now even when we restrict them to being real quantities, this gives a quite impracticably large field of choice—for three degrees there are three arbitrary parameters, for four there are six and so on, and when the coefficients may be complex the number is still larger. So there is no hope in applying the general transformation and at the end selecting particular simplifying values. Under these conditions we naturally take the doublet as guide and try to find a special transformation which will have the same features. In the first place we have to arrange for the lines without field. This we should attempt by a modification of the potential energy only, and the  $x$  direction can be treated alone. The first difficulty is to choose the number of variables, because there does not appear to be any simple way of expanding the number during the work. As a lower limit we can take the number of Zeeman components, but it is always possible (as happens in the  $\Pi$  component of a doublet) that the introduction of blind vibrations would simplify the expressions. To have a satisfactory system the one parameter which determines the intervals of the multiplet must occur in  $L$  multiplying an expression which only involves simple arithmetical coefficients. The semi-normal form would fulfil this condition, but not well, as it would fail to link together the different variables, and would have just the same form even if the separate intervals were not related. If, further, we introduce the principle that there shall be only one active electron it is definitely ruled out, since the semi-normal form requires a force factor for each line proportional to the square root of its intensity.

I have tried two methods of discovering models which obey these rules. The first is to make up determinants having certain rows so arranged that by subtraction a factor could be taken out, the constants being adjusted so that all the roots come right. Even if this could be done there would remain the probability that the force factors would not correspond to one single active electron; but, as a matter of fact, I have not succeeded in finding any determinant of this type for either a  $1s\text{-}mp$  triplet or a  $2p\text{-}md$  doublet\*. All attempts seem to require the determinant to have some root much further from the rest than is given by any of the lines, so that to use the method there would have to be some

\* In this case there would be two parameters, corresponding to the separations of the  $p$  and  $d$  terms respectively.

rather elaborate condition so as to blind this root. The second method has the advantage of certainly producing an answer of some kind. This is to construct a complete set of mutually orthogonal coefficients, selecting them as far as possible to avoid anything but simple numbers. The difficulty in this method is that the coefficients always must involve square roots, and that while they are being constructed it is very hard to see which will lead to the simplification of the coefficients in the potential energy. We shall give later an example of this process, so that it need not be further elaborated here.

To form a model for the Zeeman effect it is best to start with the semi-normal form. Then for each line of the multiplet there will be a set of relations for the  $h$ 's and further relations for the  $e$ 's. These may be insufficient to determine them completely and we choose the simplest conditions that can be found. When these are fixed we must put in the strong conditions, which give equations limiting the values of the  $h$ 's interrelating different members of the multiplet. There will not usually be enough relations to fix them completely and we must guess the rest to help the simplification. A knowledge of the frequencies in intermediate fields would decide some of these arbitrary values. When all the coefficients have been determined we have lastly to transform the whole to the form in which the potential energy is modified.

We shall illustrate the procedure by two examples. The first gives a model for the  $\Pi$  components of a doublet without the blind solutions of Voigt. The second gives the whole process for the  $\perp$  components of a normal triplet.

### 13. *An Alternative Model for the $\Pi$ Components of the D Lines.*

The D lines have in all four  $\Pi$  components, and so we must have at least four variables to represent them. We therefore take a form in  $z$  like (6.7), and add on to it terms in  $z_4$  which give the frequency of  $D_1$  when there is no field. We make  $z_4$  blind so that the intensities will be unaffected. To this expression we then add on the general form for the gyroscopic terms. Then  $L$  is

$$\left. \begin{aligned} & \frac{1}{2} \Sigma_1^4 (\dot{z}_r^2 - p_0^2 \dot{z}_r^2) + 2\beta p_0 (z_1 \dot{z}_2 + z_1 \dot{z}_3 + z_2 \dot{z}_3 + 2z_4^2) \\ & + Ze z_1 + \omega \Sigma_r \Sigma_s c_{rs} \dot{z}_r \dot{z}_s \quad (c_{sr} = -c_{rs}). \end{aligned} \right\} \quad (13.1)$$

The strong condition at once requires that  $c_{1r}$  should vanish

for all  $r$ . We next have to fit in the weak effect. The period equation for  $p = p_0 + \kappa$  is

$$\begin{vmatrix} \kappa, & \beta, & \beta, & 0 \\ \beta, & \kappa, & \beta - i\omega c_{23}, & -i\omega c_{24} \\ \beta, & \beta + i\omega c_{23}, & \kappa, & -i\omega c_{34} \\ 0, & i\omega c_{24}, & i\omega c_{34}, & \kappa + 2\beta \end{vmatrix} = 0. \quad (13.2)$$

The determinant only involves  $\omega^2$ , so the roots will be symmetrical about  $D_1$  and  $D_2$ . We are to have a root at  $p = p_0 + \beta + \frac{1}{3}\omega$ . Substitute this value and make the determinant vanish to the first order in  $\omega$ . This requires that  $c_{23}^2 = \frac{1}{3}$ . Next put  $p = p_0 - 2\beta + \frac{2}{3}\omega$ , and in the same way we find that the determinant only vanishes if  $(c_{24} + c_{34})^2 = \frac{4}{3}$ . All conditions as to frequency are satisfied, but in view of the symmetry in the coordinates  $z_2$  and  $z_3$ , we naturally take  $c_{24} = c_{34}$ . Thus we have  $c_{23} = c_{24} = c_{34} = \frac{1}{\sqrt{3}}$  (the ambiguity of sign is unimportant as it depends on arbitrary signs of the variables  $z_2, z_3, z_4$ ). Thus the gyroscopic terms are

$$\frac{\omega}{\sqrt{3}} (\dot{z}_2 z_3 - z_2 \dot{z}_3 + \dot{z}_2 z_4 - z_2 \dot{z}_4 + \dot{z}_3 z_4 + z_3 \dot{z}_4). \quad (13.3)$$

The intensities are of course correct, since in the weak field they are dictated simply by the values for no field. As a matter of fact, analysis shows that for all strengths of field the frequencies and intensities are exactly the same as those given by Voigt's model.

This model raises two points of interest. In the first place we have made the arbitrary choice that  $c_{24} = c_{34}$ . If we take other values subject to  $c_{24} + c_{34} = \frac{2}{\sqrt{3}}$  we obtain as period equation

$$(\kappa - \beta)^2 (\kappa + 2\beta)^2 = \omega^2 [\kappa^2 + \theta (\kappa - \beta) (\kappa + 2\beta)]$$

where  $\theta$  is arbitrary. Only if  $\theta = 0$  can this be split into two quadratics, except in the limit when  $\omega$  is small. So the general form will involve as frequencies the roots of an irreducible quartic. If Landé's formulæ for intermediate fields are right it might be possible to get a model giving a closer approximation by a suitable choice of  $\theta$ ; but as there is only one adjustable parameter, it seems most unlikely that the improvement would extend very far. The other point to observe is that the irrationality  $\sqrt{3}$  which we got rid of in our transformation of the  $\perp$  model has reappeared again.

This suggests that in other cases as well the introduction of blind roots may be able to reduce complicated expressions to much simpler forms. As there is nothing to tell us what values are to be taken for these blind roots, this fact is not very helpful in the actual designing of models.

#### 14. *The Triplet without Field.*

We now consider the design of a model for a triplet. The first task is to find the model for the undisplaced lines. These have separations in the ratio 1 : 2, and intensities in the ratios 1 : 3 : 5. Referring them to the centre of gravity, we thus have roots at  $p_0 - 2\beta$  with a force factor  $\frac{e}{3}$ , others at  $p_0 - \beta$  with factor  $\frac{e}{\sqrt{3}}$ , and others at  $p_0 + \beta$  with  $\frac{\sqrt{5}e}{3}$  \*.

The Zeeman effect prescribes six as the minimum number of degrees of freedom, one for the first root, two for the second, and three for the third. We shall only use this number, but may note that there is some indication that nine would be better. One reason is that the sum of the intensities adds up to 9, just as in the doublet the sum of the intensities adds up to 3, and another reason will be given below. The calculation for 9 degrees with 3 vibrations blind is, however, too impossibly heavy to pursue.

We therefore proceed to construct an orthogonal set of real coefficients of six rows, which must obey the following conditions. The period equation is to reduce to

$$(\kappa + 2\beta)(\kappa + \beta)^2(\kappa - \beta)^3 = 0.$$

The force factors in the normal form are to be

$$\frac{1}{3}, \frac{1}{\sqrt{3}}, 0, \frac{\sqrt{5}}{3}, 0, 0.$$

There is no loss of generality in taking three of them zero in this way, and it will have no effect on the algebraic form of  $L$  from which the motion is derived. These conditions are absolute. In addition we have to try as far as possible to build a form like that of the doublet. In the first place we take only one electron active and make the five others blind. This at once determines the first row of the orthogonal coefficients by (5.12) and therefrom the coefficient  $b_{11}$  (substituting  $b$  for  $h$  in (5.11)). We next have to compose the second row of coefficients. Here the choice is very wide,

\* In the absence of experimental evidence we are assuming that only one electron is active. This fits in best with the quantum theory, but there remains the possibility that both valence electrons should be active.

so we take as many of them zero as possible. The values adopted are then used to calculate  $b_{12}$  and  $b_{22}$ . Trials are made until values are found which make them simple in form. A particular guide which I used in selecting the coefficients was that the coefficients of the square terms  $b_{rr}$  should vanish, as they do in the doublet. The argument for this is not very cogent, but it seems natural to regard the coefficient of a square term as really going with the main term in  $p_0^2$  and so describing a period different from the rest, and there seems no reason that such a new period should have a simple arithmetical relation to the coefficients of product terms. Unfortunately it is not possible to be consistent in this last rule, for with six degrees we can see that at least one square coefficient cannot vanish. By (5.11)

$$\begin{aligned}\sum_r b_{rr} &= \sum_r \sum_a \kappa_a l_{ra} l_{ra} \\ &= \sum_a \kappa_a = -\beta.\end{aligned}$$

It is this fact that suggested the appropriateness of using nine degrees of freedom, for in that case all the square coefficients can vanish. However, even though we do not get a theoretical justification for the choice, it is still most useful in helping to decide between a great number of otherwise perfectly indifferent choices. Proceeding on these lines I have constructed orthogonal systems of which the following is perhaps the simplest:

	$u_1.$	$u_2.$	$u_3.$	$u_4.$	$u_5.$	$u_6.$
$x_1$	1/3	1/√3	0	√5/3	0	0
$x_2$	0	0	1/√2	0	1/√2	0
$x_3$	0	0	1/√2	0	-1/√2	0
$x_4$	1/3	1/√3	0	-4/3√5	0	1/√5
$x_5$	-1/√3	0	0	1/√15	0	3/√15
$x_6$	2/3	-1/√3	0	1/3√5	0	1/√5
$p-p_0$	-2β	-β	-β	β	β	β

(14.1)

From these we construct the potential energy by means of (5.11).

Finally the Lagrangian function is

$$\begin{aligned}\frac{1}{2} \sum_1^6 (\dot{x}_r^2 - p_0^2 x_r^2) - 2\beta p_0 [-x_2 x_3 - x_1 x_4 \\ + \frac{1}{\sqrt{3}} (x_1 + x_4 + 2x_6) x_5 - \frac{1}{2} x_6^2] + e X x_1, \quad (14.2)\end{aligned}$$

and this will give rise to the triplet with correct intervals and intensities. One or two other forms were also constructed, but none was free from irrationalities. There is no claim that the form represents any sort of physical reality, but for the sake of illustration we shall use it in dealing with the Zeeman effect.

### 15. *The Zeeman Effect of the Triplet.*

The frequencies of the components of the Zeeman effect have long been known, and recently the intensities have been conclusively fixed by theoretical principles\*, though apparently they have not been verified experimentally. We are only going to treat of the  $\perp$  components and these are given in the following scheme:—

Frequency .....	$-2\beta \pm 2\omega$	$-3 \pm \frac{3}{2}\omega$	$-\beta \pm 2\omega$	$\beta \pm \omega$	$\beta \pm \frac{3}{2}\omega$	$\beta \pm 2\omega$
Intensity .....	1	$\frac{3}{2}$	$\frac{3}{2}$	3	$\frac{3}{2}$	$\frac{1}{2}$

These are, of course, the weak effect, and to find the model we shall start with the semi-normal form, and use equations like (7.8) involving  $x + iy = \zeta$ . The equations of motion then fall into three groups, the first in  $\zeta_1$ , the second in  $\zeta_2, \zeta_3$ , and the third in  $\zeta_4, \zeta_5, \zeta_6$ . From the weak effect we determine relations for the  $h$ 's within each group. Also as we have already worked out an orthogonal system which we intend to use subsequently, we lay down that our  $\zeta$ 's are to have force factors  $\frac{1}{3}, \frac{1}{\sqrt{3}}, 0, \frac{\sqrt{5}}{3}, 0, 0$ .

The motion of  $\zeta_1$  must then be †

$$\ddot{\zeta}_1 + (p_0 - 2\beta)^2 \zeta_1 - 2i\omega(1 + h_{11})\dot{\zeta}_1 = \frac{1}{3}eZ, \quad (15.1)$$

or if  $p = p_0 + \omega + \kappa$  and  $\zeta_1, Z$  vary as  $e^{ipt}$ ,

$$2p_0\zeta_1(-\kappa - 2\beta + \omega h_{11}) = \frac{1}{3}eZ.$$

The period equation is to be

$$\kappa = -2\beta + \omega \text{ and so } h_{11} = 1. \quad (15.2)$$

The intensity is, of course, correct for a line standing alone like this.

The motion of  $\zeta_2, \zeta_3$  is given by

$$\left. \begin{aligned} \ddot{\zeta}_2 + (p_0 - \beta)^2 \zeta_2 - 2i\omega[1 + h_{22})\dot{\zeta}_2 + h_{23}\dot{\zeta}_3] &= \frac{1}{\sqrt{3}}eZ, \\ \ddot{\zeta}_3 + (p_0 - \beta)^2 \zeta_3 - 2i\omega[h_{32}\dot{\zeta}_2 + (1 + h_{33})\dot{\zeta}_3] &= 0. \end{aligned} \right\} \quad (15.3)$$

\* Ornstein & Burger, *Z. f. P.* xxviii. p. 135 (1925).

† The signs of  $\omega$  and the  $h$ 's happened to be changed in this work, but it appeared unnecessary to alter them into conformity with § 7.

In the same way these reduce to

$$\left. \begin{aligned} 2p_0\zeta_2(-\kappa-\beta+\omega h_{22})+2p_0\zeta_3\omega h_{23} &= \frac{1}{\sqrt{3}}eZ, \\ 2p_0\zeta_3\omega h_{23}+2p_0\zeta_3(-\kappa-\beta+\omega h_{33}) &= 0. \end{aligned} \right\} \quad (15.4)$$

The period equation is

$$\begin{vmatrix} -\kappa-\beta+\omega h_{22} & \omega h_{23} \\ \omega h_{32} & -\kappa-\beta+\omega h_{33} \end{vmatrix} = 0,$$

and this is to have roots  $\kappa+\beta=\frac{1}{2}\omega$ ,  $\omega$  with equal intensities. Thus  $h_{22}+h_{33}=\frac{3}{2}$  and  $h_{22}h_{33}-h_{23}h_{32}=\frac{1}{2}$ . To determine the intensities we find the normal coefficients for each frequency, and get

$$\zeta_2 = -\sqrt{2h_{33}-1} u_2 + \sqrt{2-2h_{33}} u_3,$$

and an expression for  $\zeta_3$  which we do not require. For equal intensities the coefficients of  $u_2$  and  $u_3$  must be equal. Hence  $h_{33}=\frac{3}{4}$ , and so  $h_{22}=\frac{3}{4}$  and  $|h_{23}|=\frac{1}{2}$ . There seems to be nothing gained by taking  $h_{23}$  complex, and so we have  $h_{23}=\frac{1}{2}$ .

The coefficients for  $\zeta_4$ ,  $\zeta_5$ ,  $\zeta_6$  are more troublesome, but must be dealt with in the same way. The period equation is cubic, and so there are three relations between the  $h$ 's to get the frequencies right. Next, with each of these frequencies in turn, we must find the normal coefficients and so determine  $\zeta_4$  as a sum of terms in  $u_4$ ,  $u_5$ ,  $u_6$  with coefficients which are functions of the  $h$ 's. The squared moduli of these coefficients must be in the ratios  $3:\frac{3}{2}:\frac{1}{2}$ , and this gives two further conditions. There are not enough in all to fix the  $h$ 's, and I have therefore merely selected a set which will satisfy all the conditions, taking them purely real for convenience. The equations become

$$\left. \begin{aligned} (-\kappa+\beta+\frac{1}{4}\omega)\zeta_4 + \frac{1}{4}\sqrt{\frac{3}{10}}\omega\zeta_5 + \frac{1}{4}\sqrt{\frac{3}{2}}\omega\zeta_6 &= \frac{\sqrt{5}}{3}eZ, \\ \frac{1}{4}\sqrt{\frac{3}{10}}\omega\zeta_4 + (-\kappa+\beta+\frac{7}{8}\omega)\zeta_5 + \frac{3}{8\sqrt{5}}\omega\zeta_6 &= 0, \\ \frac{1}{4}\sqrt{\frac{3}{2}}\omega\zeta_4 + \frac{3}{8\sqrt{5}}\omega\zeta_5 + (-\kappa+\beta+\frac{3}{8}\omega)\zeta_6 &= 0. \end{aligned} \right\} \quad \dots \dots \dots (15.5)$$

The next stage is to bring in the strong effect, which depends on the coefficients  $h_{12}$ ,  $h_{14}$ ,  $h_{25}$ , etc. We have relations

$$\frac{1}{3}h_{11} + \frac{1}{\sqrt{3}}h_{12} + \frac{\sqrt{5}}{3}h_{14} = 0, \text{ etc.,}$$

from (7.11) These are quite insufficient to determine all



the  $h$ 's. I therefore proceeded differently. Leaving them all undetermined the equations were transformed by means of (14.1) to their final form, a very heavy piece of work, and then the conditions become simply that in the new equations  $h_{1r}=0$ . The remaining undetermined values were chosen to be all real, and so as to remove as far as possible the irrationalities in the expressions. It is possible that the choice could be improved, but as the whole cannot be supposed to have any real physical foundation it was not worth going through the considerable labour of hunting for better values. The final equations are given; it would be quite straightforward to put down the  $L$  from which they are derived.

$$\begin{aligned}
 & \zeta_1(-\kappa) + \zeta_4(-\beta) + \zeta_5\left(\frac{\beta}{\sqrt{3}}\right) = \epsilon Z, \\
 & \zeta_2(-\kappa + \omega) + \zeta_3\left(-\beta - \frac{1}{16}\omega\right) + \omega\zeta_4\left(-\frac{3\sqrt{3}}{40} + \frac{3}{40\sqrt{2}}\right. \\
 & \quad \left. + \frac{1}{4}\sqrt{\frac{3}{2}}\right) + \omega\zeta_5\frac{1}{10}\sqrt{\frac{3}{2}} + \omega\zeta_6\frac{3\sqrt{3}}{40} = 0, \\
 & \zeta_2\left(-\beta - \frac{1}{16}\omega\right) + \zeta_3\left(-\kappa + \frac{5}{8}\omega\right) + \omega\zeta_4\left(\frac{3\sqrt{3}}{40} - \frac{3}{40\sqrt{2}}\right. \\
 & \quad \left. + \frac{1}{4}\sqrt{\frac{3}{2}}\right) + \omega\zeta_5\left(-\frac{1}{10}\sqrt{\frac{3}{2}}\right) + \omega\zeta_6\left(-\frac{3\sqrt{3}}{40}\right) = 0, \\
 & \zeta_1(-\beta) + \omega\zeta_2\left(-\frac{3\sqrt{3}}{40} + \frac{3}{40\sqrt{2}} + \frac{1}{4}\sqrt{\frac{3}{2}}\right) + \omega\zeta_3\left(\frac{3\sqrt{3}}{40}\right. \\
 & \quad \left. - \frac{3}{40\sqrt{2}} + \frac{1}{4}\sqrt{\frac{3}{2}}\right) + \zeta_4\left[-\kappa + \omega\left(\frac{21}{40} - \frac{3}{10}\sqrt{\frac{3}{2}}\right)\right] \\
 & \quad + \zeta_5\left[\frac{\beta}{\sqrt{3}} + \omega\left(-\frac{\sqrt{3}}{40} - \frac{9}{20\sqrt{2}}\right)\right] + \omega\zeta_6\left(-\frac{3}{40}\right) = 0, \\
 & \zeta_1\left(\frac{\beta}{\sqrt{3}}\right) + \omega\zeta_2\frac{1}{10}\sqrt{\frac{3}{2}} + \omega\zeta_3\left(-\frac{1}{10}\sqrt{\frac{3}{2}}\right) + \zeta_4\left[\frac{\beta}{\sqrt{3}}\right. \\
 & \quad \left. + \omega\left(-\frac{\sqrt{3}}{40} - \frac{9}{20\sqrt{2}}\right)\right] + \zeta_5\left(-\kappa + \frac{11}{40}\omega\right) \\
 & \quad + \zeta_6\left[\frac{2}{\sqrt{3}}\beta + \omega\left(-\frac{\sqrt{3}}{8} + \frac{9}{20\sqrt{2}}\right)\right] = 0, \\
 & \omega\zeta_2\frac{3\sqrt{3}}{40} + \omega\zeta_3\left(-\frac{3\sqrt{3}}{40}\right) + \omega\zeta_4\left(-\frac{3}{40}\right) \\
 & \quad + \zeta_5\left[\frac{2}{\sqrt{3}}\beta + \omega\left(-\frac{\sqrt{3}}{8} + \frac{9}{20\sqrt{2}}\right)\right] \\
 & \quad + \zeta_6\left[-\kappa - \beta + \omega\left(\frac{63}{40} + \frac{3}{10}\sqrt{\frac{3}{2}}\right)\right] = 0. \\
 & \quad \quad \quad \dots (15.6)
 \end{aligned}$$

In these equations  $\kappa$  stands for  $p - p_0 - \omega$ . We cannot claim any physical reality for them; but merely that they do satisfy all the known conditions of a triplet while having only one active electron, after the manner suggested by the quantum theory.

The general balance of evidence would seem to be against the physical significance of mechanical models. We have seen how Voigt's model can be transformed in such a way that it can be given a physical meaning—at any rate as significant as is possible within the limitations of the classical theory; but this success is vitiated by its failure to accommodate Landé's calculations of the frequencies in fields of intermediate strength. The behaviour of such lines as the mercury line  $1S-2p$  can definitely not be explained by a similar model, without introducing complications which would destroy much of its simplicity; and the magnetic gyration of ordinary substances also raises difficulty. Finally, though not conclusively, I have had no success in obtaining arithmetical simplicity for the corresponding model of the triplet.

On the other hand, it is possible to construct more general types of model which will meet these difficulties and which are mathematically useful in the calculation of gyration. They suggest the possibility of experiments which, using fields of practicable strength, should yield new information about the optical effects of magnetism.

Edinburgh, May 1925.

XII *On the Analysis of Certain Molecular Spectra.* By  
DAVID M. DENNISON, *Ph.D.*, *University of Michigan* \*.

IN recent years much important work has been accomplished in interpreting molecular spectra by means of the quantum theory, and especially in obtaining information regarding the structure of the molecule through an examination of the positions and fine structure of the infra-red bands. Somewhat further light may be thrown upon this question through a consideration of the intensities of the bands with the aid of the correspondence principle.

In a recent article † I have investigated the molecular vibrations and infra-red spectrum of  $\text{CH}_4$ , and in this paper it

\* Communicated by Prof. N. Bohr.

† D. M. Dennison, *Astrophys. Journ.* lxii. p. 84 (1925)

is intended to discuss from a similar point of view the infra-red spectra of the hydrogen halides, of  $\text{CO}_2$ , and of  $\text{NH}_3$ . No attempt has been made in this work to enter into the question of the origin of the forces holding the molecule in equilibrium, but the assumption has been made that the behaviour of the nuclei in the neighbourhood of their equilibrium positions may be described by means of central forces acting between them. This assumption, which is rigorously valid for the diatomic molecules, imposes in the case of a polyatomic molecule certain limitations in regard to the character of the equilibrium of the system. For the molecules considered in this note, where the number of degrees of vibrational freedom is just equal to the number of lines connecting the nuclei, the assumption as to central forces imposes the condition that there shall exist an equilibrium of the forces between each pair of nuclei. It is thought that the examination of the motion of such a simple model may suffice for the general interpretation of the character of the vibration to be associated with each band.

### § 1. *Molecular Vibrations.*

The bands of the infra-red spectra as observed experimentally are found to consist of finite regions of absorption which in certain cases have been resolved into a series of fine structure lines due to the rotation of the molecule. It is easily shown\* that the integral of the observed absorption coefficient  $\alpha_\nu$  over the region of the band in question is connected in the following way with the Einstein probability coefficient  $A_0^i$  of spontaneous transition from the state  $\nu_i$  to the normal or vibrationless state,

$$A_0^i = \frac{g_0}{g_i} \nu_i^3 K \int_0^\infty \alpha_\nu d\nu,$$

where  $g_0$  and  $g_i$  are the *a priori* probabilities of the normal state and of the state  $\nu_i$  respectively, and  $K$  is independent of  $\nu_i$ . Since the absorption coefficient  $\alpha_\nu$  is the quantity which is observed experimentally, it will be convenient to employ as a measure of intensity  $\rho_i^2$ , defined by the relation

$$\rho_i^2 = \frac{A_0^i}{\nu_i^2} = \frac{g_0}{g_i} K \int_0^\infty \alpha_\nu d\nu. \quad . \quad . \quad . \quad (1)$$

In many cases, due to the experimental difficulties in

\* Füchtbauer, *Phys. Zeit.* xxi. p. 322 (1920); R. Tolman, *Phys. Rev.* xxiii. p. 693 (1924).

determining the form of the absorption curves, it is inaccurate to compute the integral of the absorption coefficient over the region. It is evident, however, that when we compare absorption bands of the same molecule for which the electric moment vibrates in the same direction, the effective moment of inertia will be the same for each band, and hence if the absorption curves are plotted to a scale of frequencies as abscissæ, they will be everywhere proportional in their ordinates. Thus, if we compare two curves of this sort, the integral may be replaced by the absorption coefficient at some characteristic point, as, for example, its maximum value  $(\alpha_\nu)_m$ . It is unfortunate that there are so few accurate data available as to the experimental values of the intensities of the infra-red bands. This is possibly due both to the difficulty in obtaining them and to the fact that in the past the greatest interest has been centered on the positions of the lines and not upon their relative intensities. For that reason the experimental values given in this paper seem in general to have an accuracy which is no better than 10 or 20 per cent., and in a few cases may well be worse.

A comparison between the experimental value of  $\rho_i^2$  as determined by (1), and a theoretical estimate of this quantity is obtained through a consideration of the motion of the electric moment of the model. In accordance with the previous assumption as to central forces acting upon the nuclei, it will now be assumed that each nucleus may be thought of as the centre of an effective charge, and that hence the change of electric moment is directly proportional to the displacement of the particles relative to the centre of gravity of the system. If  $E_i$  be the amplitude of the change of the electric moment, as is well known, the correspondence principle yields the following relation which in general is rigorously valid only in the region of large quantum numbers :

$$A_0^i(h\nu_i) = gE_i^2\nu_i^4;$$

and hence

$$\rho_i^2 = \frac{A_0^i}{\nu_i^2} = E_i^2\nu_i(\text{const.}) \quad . \quad . \quad . \quad (2)$$

In using this equation in the following sections it will be assumed that the amplitude of the change of the electric moment  $E_i$  is to be taken in the upper state rather than an average value between the two states to be connected with the transition. Such a procedure seems to be entirely justified in comparing the intensities of the fundamental vibration bands of a given system, since the relative values

of  $\rho_i^2$  will be approximately independent of any type of average of  $E_i$  which might be taken. On the other hand, in comparing the intensity of a fundamental with that of its harmonics, appreciable errors may enter due to this cause, but it has been thought best even here to use the value of  $E_i$  in the upper state since in all cases the transition is to the zero or vibrationless state.

In considering the general characteristics of the vibratory motion of a molecule, an essential simplification of the problem may be made by assuming the amplitude of vibration to be infinitesimal; an assumption which, as is well known from the experimental positions of the harmonic bands of diatomic and other molecules, will not introduce any appreciable errors as regards the values of the fundamental frequencies. A system of  $n$ -particles will in general have  $3n$  degrees of freedom, but of these three degrees may be associated with a translation of the system as a whole and (for  $n > 2$ ) three degrees with a rotation of the system, and hence there are left only  $3n - 6$  degrees of internal or vibrational freedom. While an analysis of the motion may be carried out using  $3n$  coordinates, it seems preferable in the present case, where the displacements of the particles are infinitely small, to use only  $(3n - 6)$  coordinates, ignoring from the outset those coordinates which define the translation and rotation of the system. Such an ignorance may easily be effected by allowing only such displacements of the particles in space for which, in an imagined state of motion where the velocities of the particles are proportional to the displacements in question, the linear and angular momenta of the system are equal to zero. Under these conditions the potential and kinetic energies may be expressed as positive definite quadratic forms in the  $(3n - 6)$  coordinates and their time derivatives respectively and, through the transformation to the so-called normal coordinates, the normal or fundamental frequencies of the system may be determined.

Since the amplitude of vibration is assumed to be infinitesimal the electric moment in any direction  $R_\theta$  may be expressed as a linear function of the  $(3n - 6)$  original coordinates, and hence also of the normal coordinates which are connected to the original coordinates by linear transformations. Thus,

$$R_\theta = \sum_1^u B_{\theta i} \cos(2\pi\nu_i t + \gamma_i),$$

where  $\nu_1, \dots, \nu_u$  are the normal frequencies. A simple application of the correspondence principle makes it evident that,

according to the quantum theory, just as in the classical theory, only the frequencies  $\nu_1, \dots, \nu_n$  may be absorbed or emitted, and that hence the system is equivalent to a number  $n$  of independent Planck oscillators whose characteristic frequencies are directly the normal frequencies of vibration. As is well known, such a simplified system does explain the essential features of the observed infra-red spectra, consisting mainly as they do of a series of prominent fundamental frequencies which are independent of each other. The appearance of harmonic and combination bands is conditioned by a divergence of the motion of the molecule from infinitesimal motion, and the problem of their intensity will be treated in the following section.

## § 2. Diatomic Molecules. Intensity of Harmonic Bands

The diatomic molecule possesses one degree of vibrational periodicity and one degree of rotational periodicity. In the first approximation, when the amplitude of vibration is taken to be infinitesimal and the moment of inertia constant during transition, the spectrum reduces to one band, the fundamental, whose fine structure consists of a series of lines linearly spaced as regards frequency. The theoretical frequencies of the harmonic bands, whose intensities are, however, zero under these assumptions, would be exact multiples of the frequency of the fundamental band. The true finite and anharmonic character of the motion is shown in the fact that the observed fine structure lines are not exactly linearly spaced, but are crowded together on one side of the band. Moreover, the harmonic bands appear with finite intensity and their frequencies are not exact multiples of the fundamental but are given by the following relation, where  $x$  is a small constant characteristic of the potential energy function :

$$\nu = n\nu_0(1 - nx).$$

As is well known, Kratzer\* has been able, by quantizing the motion of a rotating anharmonic oscillator, to account satisfactorily for the positions of the fine structure lines, and from the observations of Imes† on the hydrogen halides to determine the potential energy function for these substances. In the present section the attempt will be made to compare the relative intensities of the fundamental and harmonics

\* A. Kratzer, *Zeit. f. Phys.* iii. p. 289 (1920).

† E. S. Imes, *Astrophys. Journ.* l. p. 251 (1919).

through the use of the constants of the potential energy function just mentioned.

Let the kinetic and potential energies be expressed as follows, where  $\mu$ ,  $K$ ,  $K_2$ , and  $K_3$  are constants, and  $X$  the normal variable representing the displacement of the nuclei from their equilibrium positions :

$$T = \frac{1}{2}\mu\dot{X}^2,$$

$$U = \frac{K}{2}X^2 + \frac{K_2}{3}X^3 + \frac{K_3}{4}X^4.$$

The following equations have been derived by Kratzer (*l. c.*) and by Hettner\*, giving the approximate solution of the energy equations :

$$X = A \cos 2\pi\nu t + \frac{K_2 A^2}{6K} \cos 4\pi\nu t \\ + \left( \frac{K_2^2}{6K^2} + \frac{K_3}{4K} \right) \frac{A^3}{8} \cos 6\pi\nu t - \frac{K_3 A^2}{2K},$$

$$\nu = \nu_0 \left\{ 1 - \frac{A^2}{24} \left[ 10 \left( \frac{K_2}{K} \right)^2 - \frac{9K_3}{K} \right] \right\},$$

$$T + U = nh\nu_0 \left\{ 1 - \frac{A^2}{48} \left[ 10 \left( \frac{K_2}{K} \right)^2 - \frac{9K_3}{K} \right] \right\} = nh\nu_0(1 - xn),$$

where  $\nu_0 = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$  and  $A^2 = \frac{nh}{2\pi^2\mu\nu_0}.$

According to equation (2) the intensities of the fundamental and first and second overtones to a high approximation become respectively, ignoring the constant,

$$\rho_1^2 = A_0^2\nu_0,$$

$$\rho_2^2 = \left( \frac{K_2}{6K} \right)^2 (4A_0^4)(2\nu_0) = \frac{2}{9} \left( \frac{K_2}{K} \right)^2 A_0^4\nu_0,$$

$$\rho_3^2 = 81 \left( \frac{K_2^2}{48K^2} + \frac{K_3}{32K} \right)^2 A_0^6\nu_0,$$

where  $A_0^2 = \frac{h}{2\pi^2\mu\nu_0}.$

In computing the above values there is involved an uncertainty which is inherent to all the usual applications of the correspondence principle to the question of intensities,

\* G. Hettner, *Zeit. f. Phys.* i. p. 351 (1920).

namely, the uncertainty as to which value of the amplitude  $E_i$  shall be used in equation (2). As has been mentioned, it has been assumed in the present work that the amplitude in the higher state is to be used, since each transition is to the zero or vibrationless state.

We may compare the theoretical intensities with the intensities found experimentally in the case of the halogen halides, through the use of equation (1).

	$\frac{K_2 A_0}{K}$	$\frac{\rho_2^2}{\rho_1^2}$ (Theo.).	$\frac{\rho_2^2}{\rho_1^2}$ (Exp.).
HBr .....	—·412	·038	·05
HCl .....	—·443	·044	·06
HF.....	—·475	·050	—

The values of  $\frac{K_2 A_0}{K}$  depend upon the experimental work of Imes (*l. c.*) for HBr and HF and upon that of Colby, Meyer and Bronk \* for HCl. The experimental value of  $\frac{\rho_2^2}{\rho_1^2}$  is obtained from the work of Brinsmade and Kemble † for HCl, while for HBr it is necessary to combine their work with that of Burmeister ‡.

Since the constant  $\frac{K_2 A_0}{K}$  depends upon a knowledge of the fine structure which is in most cases unknown, it is impossible to test the intensities generally by the methods given above. There does, however, exist a relation between  $\rho_1^2$ ,  $\rho_2^2$ ,  $\rho_3^2$  and  $x$ , which may in certain cases be tested experimentally. Thus the position of the centre of each band  $\nu_i$  is given by

$$\nu_i = \nu_0 n_i (1 - x n_i),$$

where evidently

$$x = \frac{A_0^2}{48} \left[ 10 \left( \frac{K_2}{K} \right)^2 - 9 \frac{K_3}{K} \right].$$

The relation between the constants in question is found by direct substitution to be

$$x = \frac{3}{2} \frac{\rho_2^2}{\rho_1^2} - \frac{2}{3} \left( \frac{\rho_2}{\rho_1} \right) \left( \frac{\rho_3}{\rho_2} \right).$$

\* Colby, Meyer & Bronk, *Astrophys. Journ.* lvii. p. 7 (1923).

† J. Brinsmade & W. C. Kemble, *Proc. Nat. Acad.* iii. p. 420 (1917).

‡ B. Burmeister, *Verh. d. D. phys. Ges.* xv. p. 589 (1913).



This formula may be tested to a certain extent in the case of CO, where, according to Burmeister (*l. c.*),

$$\alpha = \cdot 006,$$

$$\frac{\rho_2^2}{\rho_1^2} = \cdot 031.$$

Hence, solving for  $\frac{\rho_3^2}{\rho_2^2}$ , we find

$$\frac{\rho_3^2}{\rho_2^2} = \cdot 12.$$

C. Schaefer and M. Thomas\* have found experimentally the second overtone of CO and give as a measure of its relative intensity 1:14·3, as compared with the first overtone.

Taking this as a measure of  $\frac{\rho_3^2}{\rho_2^2}$ , we have,

$$\frac{\rho_3^2}{\rho_2^2} = \cdot 07.$$

### § 3. *Symmetrical Triatomic Molecules.*

In considering the vibration spectrum of a triatomic molecule of the general type  $XY_2$ , it does not seem possible, without some further assumption as to the structure, to determine uniquely the form of the molecule from the positions of the fundamental infra-red bands whose number is at most three. In the present treatment it will be assumed that the Y-atoms are equidistant from the X-atom, and that in general the three atoms do not lie along a straight line. Such an assumption does not seem inconsistent with the general chemical and physical evidence as to the structure of such molecules and in the case of  $H_2O$  is directly in accord with a recent investigation by Hund†, in which the equilibrium states of this molecule among others were examined under the assumption that the electronic configuration is central about the oxygen nucleus, with the exception of a polarization induced by the presence of the hydrogen nuclei.

If the assumption mentioned previously is made, that the fields of force are central about each atom, the potential

\* C. Schaefer & M. Thomas, *Zeit. f. Phys.* xii. p. 330 (1923).

† F. Hund, *Zeit. f. Phys.* xxxi. p. 81 (1925).

energy function for infinitesimal displacements reduces to the following simple form :

$$W = \frac{K}{2} q_1^2 + \frac{K'}{2} (q_2^2 + q_3^2),$$

where  $K$  and  $K'$  are constants,  $q_1$  the mutual displacement of the Y-particles relative to each other, and  $q_2$  and  $q_3$  the mutual displacements of the X-particle relative to each Y-particle respectively. As original coordinates it has, however, been found more convenient to choose  $q$ ,  $x$ ,  $y$ , where  $q$  is equal to  $q_1$  as just defined, and  $x$  and  $y$  are the displacements in rectangular coordinates of the X-particle relative to the centre of gravity of the Y-particles. Let  $M$  be the mass of the X-particle, and  $m$  that of each Y-particle, and let  $\alpha$  be the half angle at the apex of the isosceles triangle formed by the three particles. The potential and kinetic energies for infinitesimal displacements may be found quite simply by allowing a variation of each coordinate to occur independently, and by examining the total resulting displacement of each particle under the conditions that there shall be no rotation or translation of the molecule as a whole. As is well known, the energy functions allow a determination of the normal frequencies of the system as a function of the roots of a characteristic determinant\*, which in the present case may be written in the following form :

$$\left[ \frac{m\lambda}{K'} - 1 - \frac{2m}{M} \sin^2 \alpha \right] \left[ \left( \frac{m\lambda}{K'} \right)^2 - 2 \left( \beta + \frac{1}{2} + \frac{m}{M} \cos^2 \alpha \right) \frac{m\lambda}{K'} + \frac{2\beta}{\mu} \cos^2 \alpha \right] = 0,$$

where

$$\beta = \frac{K}{K'}$$

and

$$\mu = \frac{M}{2m + M}.$$

The system is evidently non-degenerate since the above determinant contains three independent roots, which we shall denote by  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  respectively, leading to three frequencies †,  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ , where

$$\nu_i = \frac{1}{2\pi} \sqrt{\lambda_i}.$$

\* See, for example, E. T. Whittaker, 'Analytical Dynamics,' 2nd edition, p. 178.

† In addition to considering the equilibrium of the molecule of  $H_2O$ , Hund (l. c.) has computed its normal frequencies of vibration under the assumptions mentioned previously. The frequency functions obtained by him may be directly transformed into the normal frequencies given here by allowing the coefficients referring to the polarization to vanish.

An examination of the character of motion to be associated with each normal mode of vibration may be made through a consideration of the linear equations connecting the so-called normal coordinates with the original coordinates  $q, x, y$ . In the motion corresponding to the vibration  $\nu_1$ , where  $\lambda_1$  is the linear root of the determinant, it is found that the X-particle vibrates in the plane of the triangle along a line perpendicular to the symmetry line while the distance between the Y-particles remains unchanged\*. In the motion corresponding to either  $\nu_2$  or  $\nu_3$  the X-particle vibrates along the line of symmetry, while the Y-particles in their motions always preserve a symmetry about this line.

As has been mentioned, the change of the electric moment is assumed to depend directly upon the displacements of the particles, and in the present case will be proportional to the displacement of the X-particle relative to the centre of gravity of the Y-particles; that is, it will have components proportional to the original coordinates  $x$  and  $y$ . The intensity  $\rho_i^2$  as defined by equation (2) may now be found, with the aid of the linear equations referred to above, to have the values

$$\rho_1^2 = \frac{C}{2\mu + \frac{2\mu^2}{\tan^2 \alpha}},$$

$$\rho_j^2 = \frac{C}{2\mu + \frac{1}{2} \left( \frac{\sin \alpha \cos \alpha}{2K_j^2 - \beta - \frac{1}{2} \sin^2 \alpha} \right)^2},$$

$$j = 2, 3.$$

The problem of the normal frequencies of the CO<sub>2</sub> molecule was attacked in a most successful manner by N. Bjerrum† in 1914 through the use of assumptions which were identical with those employed here, and which lead to identical frequency functions. By correlating the observed spectrum of CO<sub>2</sub> with the theoretical frequencies he obtained two solutions yielding two very different values for  $\alpha$ —72°·5 and 20°·3,—between which he was not able to decide at that time. It is found upon computing the intensities that the latter solution,  $\alpha = 20^\circ\cdot3$ , is entirely inconsistent with the experimental data, whereas the theoretical values for the intensities seem in quite good agreement with

\* It is to be noted that  $K$  does not enter the expressions for  $\nu_1$ .

† N. Bjerrum, *Verh. d. D. phys. Ges.* xvi p. 737 (1914).

experiment under the former solution, where  $\alpha = 72^{\circ}5$ , and in the following work only this solution will be considered.

Many investigators have examined the near infra-red spectrum of  $\text{CO}_2$  and have found it to consist of three bands lying at  $2.74 \mu$ ,  $4.25 \mu$  and  $14.66 \mu$ , with almost no absorption between these regions. In the following, the work of W. W. Coblentz \* will be used both for determining the positions of the bands and their relative intensities as given by equation (1). Since there are three constants— $K$ ,  $K'$ , and  $\alpha$ —the positions of the three bands are just sufficient for their determination.

The constants entering the intensity expressions are so chosen that the sets agree at the longest wave-band :

$$\alpha = 72^{\circ} 37',$$

$$K = 554 \times 10^4,$$

$$K' = 151 \times 10^4.$$

	Frequency (Theo.).	Frequency (Obs.).	Direction of vibra- tion of electric moment relative to symmetry line.	$\rho_i^2$ (Theo.).	$\rho_i^2$ (Obs.).
$\nu_1$ .....	$705 \times 10^{11}$	$705 \times 10^{11}$	I	1.8	2.0
$\nu_2$ .....	$1095 \times 10^{11}$	$1095 \times 10^{11}$	II	0.01	0.5
$\nu_3$ .....	$205 \times 10^{11}$	$205 \times 10^{11}$	II	1.8	1.8

The agreement between the theoretical and observed frequencies is, of course, no direct verification of the theoretical model, since there are just as many constants entering the theoretical expressions as there are frequencies. On the other hand, the values of the relative intensities depend only upon the constants  $K$ ,  $K'$ , and  $\alpha$ , which have been entirely determined from the positions of the bands. It is seen that the theoretical prediction of two strong bands  $\nu_1$  and  $\nu_3$ , of about equal intensity, and one weak band  $\nu_2$  is qualitatively in accord with the observations, although the exact value of the intensity of this latter is somewhat in error. While this is no doubt due mainly to a failure of the theoretical assumptions, it may also in some degree be due to the experimental difficulty of determining accurately the intensity of a very weak band.

Before turning to the question of the fine structure of the

\* W. W. Coblentz, 'Investigations of Infra-red Spectra,' Part I., Carnegie Institute of Washington, D. C. (1905).

CO<sub>2</sub> bands, a few remarks may be made concerning the type of molecule predicted by the above correlation. Unfortunately, the number of observed bands does not decide between a symmetrical and a non-symmetrical model, since either in general possesses three independent frequencies of vibration. In the particular case, however, when the three atoms lie in a straight line with the oxygens symmetrically placed on either side of the carbon, the change of electric moment for one of the three vibrations will be zero, provided only the symmetry extends to the potential energy function, since for this vibration the original symmetry of the model is preserved at every instant in the motion. Thus the fact that three bands of finite intensity are observed seems to remove the possibility that the particles can be symmetrically located along a straight line.

On the other hand, from measurements of the dielectric constant of CO<sub>2</sub>, H. Weigt\* has determined the electric moment of the molecule in the normal state and has found it to have a very small value—about  $\frac{1}{15}$  the corresponding value for the HCl molecule. This result seems to give a certain support to the theoretical model, since if  $\alpha$  has a value as large as 72°·5, the carbon atom is not greatly displaced from the line of the oxygen atoms, and hence the electric moment might be expected to have a small value as compared, for example, with the electric moment of HCl.

While nothing definite can be said with regard to the values of  $K$  and  $K'$ , it may be of interest to compare the value of  $K'$  for the carbon-oxygen bond in CO<sub>2</sub> with the value of  $K'$  for the bond in carbon monoxide. Such a comparison is only justified in the sense that if the fields of force are central in CO<sub>2</sub>, then there must exist an equilibrium of the forces between each two particles just as for the case of a diatomic molecule, and hence to a first approximation the potential energy function may be the same for the C—O bond in both CO<sub>2</sub> and CO. The spectrum of CO consists of one fundamental band at  $4.66\mu$  and its harmonics. The constant  $K'$  may be found from the following equation, where  $\mu$  is the reduced mass of the carbon and oxygen atoms:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K'}{\mu}}.$$

Substituting, we find  $K' = 184 \times 10^4$ , a value which is in quite fair agreement with the corresponding value  $K' = 151 \times 10^4$  deduced from the CO<sub>2</sub> spectrum.

\* H. Weigt, *Phys. Zeit.* xxii. p. 643 (1921).

E. F. Barker\* has investigated with high dispersion the bands corresponding to  $\nu_1$  and  $\nu_2$ . The second of these at  $4.25\mu$  he found to consist of a rather close doublet, the distance between whose maxima he gives to be  $9.12 \times 10^{11}$  waves per sec. The band at  $2.74\mu$  was resolved into four maxima giving the appearance of two doublets. The position of these maxima, which seem in themselves about to be resolved into fine lines, he gives to be 1080.7, 1089.7, 1111.9, and  $1120.6 \times 10^{11}$  waves per sec.

In the theoretical model considered above, where  $\alpha = 72^\circ 37'$ , the principal moments of inertia have the following values where  $A$  is the moment of inertia about the axis, lying in the plane of the particles and perpendicular to the symmetry line :

$$\begin{aligned} A &= A, \\ B &= 37.4 A, \\ C &= 38.4 A. \end{aligned}$$

It is clear that to a first approximation the model may be thought of as possessing an axial symmetry about the  $A$ -axis, which we shall now call the figure-axis. As is well known, the quantum conditions become very simple when  $B=C$  and the rotational energy assumes the following value :

$$E_r = \left[ \frac{m^2}{C} + \left( \frac{1}{A} - \frac{1}{C} \right) n^2 \right] \frac{h^2}{8\pi^2},$$

where

$$n \leq m.$$

Consider first the band  $\nu_1$  at  $4.25\mu$ . The electric moment, according to the theoretical model, vibrates along the figure-axis, and an expansion of the motion in a trigonometric series shows, with the aid of the correspondence principle, that only the following transitions may occur † :

$$\begin{cases} \Delta m = 0, \\ \Delta n = 0, \end{cases} \quad \begin{cases} \Delta m = \pm 1, \\ \Delta n = 0. \end{cases}$$

The first of these sets of transitions would give rise to a zero branch, but it is easily seen that the intensities of its lines are proportional to  $\frac{n^2}{m^2}$ , whereas the intensities of the

\* E. F. Barker, *Astrophys. Journ.* lv. p. 391 (1922).

† The complete expansion of the motion in a trigonometric series appears in the author's paper on methane, mentioned previously.

lines to be associated with the second set of transitions are proportional to  $\frac{m^2 - n^2}{m^2}$ . On account of the fact that  $\frac{1}{A} \gg \frac{1}{C}$ , it is evident, from the function for  $E_r$ , that in a state of temperature equilibrium the most probable values for  $n$  will be very much smaller than those for  $m$ , and hence it is to be expected that the total intensity of the zero branch will be very small and might well have escaped Barker's observations. On the other hand, the second set of transitions gives rise to a positive and negative branch not unlike the fine structure observed for the diatomic gases. While Barker was unable to resolve the individual lines, he was able to compute the moment of inertia in the well-known manner from the separation of the maxima of intensity of the two branches. He gives the following result:—

$$B \cong C \cong 48.6 \times 10^{-40} \text{ gm. cm.}^2.$$

Using this value in conjunction with that of  $\alpha$  obtained from the theoretical model, we may compute the distance between the oxygen nuclei to be  $1.92 \times 10^{-8}$  cm. and the distance between the carbon nucleus and the centre of gravity of the oxygen nuclei to be  $0.30 \times 10^{-8}$  cm.

In the motion corresponding to the band  $\nu_2$  at  $2.74 \mu$ , the model predicts that the electric moment vibrates perpendicular to the figure-axis. It may be shown that the only possible transitions are,

$$\begin{cases} \Delta m = 0, \\ \Delta n = \pm 1, \end{cases} \quad \begin{cases} \Delta m = \pm 1, \\ \Delta n = \pm 1, \end{cases}$$

giving rise to the following sets of lines:

$$\nu = \left( \frac{1}{A} - \frac{1}{C} \right) (\pm 2n + 1) \frac{h}{8\pi^2},$$

$$\nu = \left\{ \frac{1}{C} (\pm 2m + 1) + \left( \frac{1}{A} - \frac{1}{C} \right) (\pm 2n + 1) \right\} \frac{h}{8\pi^2}.$$

These lines may evidently be thought of as a series of lines whose spacing is  $\left( \frac{1}{A} - \frac{1}{C} \right) \frac{h}{4\pi^2}$ , upon which spacing is superimposed a second set of lines of spacing  $\frac{1}{C} \frac{h}{4\pi^2}$ . This corresponds well with the observed fine structure when we remember that  $\frac{1}{A} \gg \frac{1}{C}$ . In correlating theory and

experiment it becomes necessary to assume that the positions of the lines of spacing  $\left(\frac{1}{A} - \frac{1}{C}\right) \frac{h}{4\pi^2}$  coincide with the centres of the two doublets, whereas each of these doublets in itself is due to the envelope of unresolved lines of spacing  $\frac{1}{C} \frac{h}{4\pi^2}$ . Such a view is strengthened by the fact that the separation of the maxima of these doublets is, within experimental error, equal to the separation of the doublet in the band at  $4.25 \mu$ , which is due wholly to lines of spacing  $\frac{1}{C} \frac{h}{4\pi^2}$ . The great energy involved in changes of the quantum number  $n$  explains why at ordinary temperatures no further lines of this series were observed. If, from analogy with the hydrogen halide spectra, we assume that the series of lines of spacing  $\left(\frac{1}{A} - \frac{1}{C}\right) \frac{h}{4\pi^2}$  has a gap of one missing line in the centre\*, the moment of inertia  $A$  may be computed to be

$$A = 1.05 \times 10^{-40} \text{ gm. cm.}^2.$$

The experimentally observed spectrum leads to a ratio  $\frac{C}{A} = 46$ , which seems to be in good agreement with the theoretical value of about 38.

#### §4. Axially Symmetrical Molecules with Four Atoms.

In the present section we shall consider the vibration spectrum of a molecule of the type  $XY_3$ . The assumption will be made that in the normal state of the molecule the X-atom is equidistant from each of the Y-atoms which themselves lie at the corners of an equilateral triangle. It is further assumed that the X-atom does not lie in the plane of the Y-atoms. If, as before, the fields of force are taken to

\* The number of missing lines at the centre cannot be ascertained until more lines of the series of spacing  $\left(\frac{1}{A} - \frac{1}{C}\right) \frac{h}{4\pi^2}$  are found experimentally. It is quite possible that there is no gap in the centre of the band, in which case the value of  $A$  will be about half that given above and the value of  $\frac{C}{A}$  will not check as well with the theoretical model.



be central about each atom, the potential energy function for infinitesimal displacements becomes

$$W = \frac{K}{2}(q_1^2 + q_2^2 + q_3^2) + \frac{K'}{2}(q_4^2 + q_5^2 + q_6^2),$$

where  $q_1, q_2$ , and  $q_3$  are the displacements of the Y-particles relative to each other, and  $q_4, q_5$ , and  $q_6$  the displacements of the X-particles relative to each of the Y-particles respectively.

As original coordinates we shall choose  $q_1, q_2, q_3$  giving the displacements of the Y-atoms relative to each other, and  $x, y, z$  giving the displacement of the X-atom along rectangular axes relative to the centre of gravity of the Y-atoms. The kinetic and potential energies for infinitesimal displacements are deduced in a manner similar to that for the triatomic model, namely, by allowing variations of the coordinates  $q_1, q_2, q_3, x, y, z$  to occur independently and by examining the total displacements of each particle both in space and relative to each other under the conditions of no rotation or translation of the system as a whole. Letting  $M$  be the mass of the X-atom,  $m$  that of each Y-atom,  $a$  the normal distance of the Y-atoms from each other, and  $c$  the normal distance of the X-atom from the plane of the Y-atoms, we find the following expression for the characteristic determinant :

$$\left[ l^2 - 2 \left( \frac{3}{2} \alpha + \frac{1}{6} + \frac{c^2}{2\mu a^2} \right) l + \frac{3\alpha c^2}{\mu a^2} \right] \left[ l^2 - 2 \left( \frac{3}{4} \alpha + \frac{1}{12} + \frac{b}{12\mu} \right) l + \frac{\alpha b}{4\mu} \right]^2 = 0,$$

where

$$l = \frac{m \left( c^2 + \frac{a^2}{3} \right) \lambda}{K' a^2}, \quad \mu = \frac{M}{3m + M},$$

$$\alpha = \frac{K}{K'} \left( \frac{c^2 + \frac{a^2}{3}}{a^2} \right), \quad \text{and} \quad b = 1 + 6\mu \frac{c^2}{a^2}.$$

The roots of the determinant we shall call  $\lambda_1, \lambda_2, \lambda_3$ , and  $\lambda_4$  respectively, where  $\lambda_3$  and  $\lambda_4$  are the double roots and where  $\lambda_1 > \lambda_2$  and  $\lambda_3 > \lambda_4$ . The system is evidently degenerate, for, while it possesses six degrees of freedom, only four independent frequencies,  $\nu_1, \nu_2, \nu_3$ , and  $\nu_4$  enter the motion\*.

\* One of the cases treated under very general assumptions by C. J. Brester ('Kristallsymmetrie und Reststrahlen,' Utrecht, 1923, p. 117) is that of the molecule considered in the present section. He finds that

where, of course,

$$\nu_i = \frac{1}{2\pi} \sqrt{\lambda_i}.$$

The linear transformations connecting the original coordinates with the normal coordinates were found in order to understand the nature of the motion corresponding to each normal mode of vibration. In the vibrations  $\nu_1$  or  $\nu_2$ , the transformations show that the X-particle vibrates along the symmetry axis, while the Y-particles in their motion always remain symmetrical with respect to this axis. Since the corresponding roots are single roots, the motion is quite determined in terms of the above constants. In the motion corresponding to  $\nu_3$  or  $\nu_4$ , the X-particle always remains in a plane perpendicular to the symmetry axis. The roots  $\lambda_3$  and  $\lambda_4$  are double roots, and hence two arbitrary constants enter the motion. It may be shown that in this motion the X-particle moves in an ellipse whose eccentricity and orientation in the symmetry plane are determined by the arbitrary constants. The family of ellipses, however, are conditioned through the relation that the sum of the squares of their minor and major axes shall be a constant, which is a function of the quantum conditions.

As in the case of the triatomic molecule, we shall assume that the change of the electric moment is proportional to the displacement of the X-particle relative to the centre of gravity of the Y-particles. The intensities as determined by equation (1) may now be computed, making use of the linear transformations referred to:

$$\rho_j^2 = \frac{\frac{c^2}{a^2} C}{3\mu \frac{c^2}{a^2} + \left[ \frac{3\mu m \left( c^2 + \frac{a^2}{3} \right) \lambda_j}{K' a^2} - \frac{3c^2}{a^2} \right]^2}$$

$$\rho_K^2 = \frac{\frac{36}{b^2} \left[ \frac{2}{3} \frac{m \left( c^2 + \frac{a^2}{3} \right) \lambda_K}{K' a^2} - \alpha - \frac{1}{9} \right]^2 C}{\frac{4}{3} + \frac{(36)3\mu}{b} \left[ \frac{2}{3} \frac{m \left( c^2 + \frac{a^2}{3} \right) \lambda_K}{K' a^2} - \alpha - \frac{1}{9} \right]^2},$$

where C is a constant.

there will exist four active frequencies—two single oscillations with electric moment vibrating along the symmetry axis, and two double oscillations—perpendicular to the axis, a result entirely in agreement with the present work.

The best existing data for a molecule of the type under consideration seem to be for the molecule of ammonia,  $\text{NH}_3$ . W. W. Coblentz (*l. c.*) has observed two very intense bands at  $10.7\mu$  and  $6.14\mu$ , with a considerably weaker band at  $2.97\mu$ , beyond which point he did not go. Lately K. Schierkolk\* has re-examined a long range of the ammonia infra-red spectrum under high dispersion. In addition to the bands cited by Coblentz, he has found a band at  $2.22\mu$  of the same order of intensity as the band at  $3.0\mu$ . Beyond this he found two bands at  $1.94\mu$  and  $1.49\mu$  whose intensity was about half that of the two bands immediately preceding. He observed, moreover, a series of very faint bands, many of which may evidently be thought of as combinations and harmonics of the intense bands†.

As has been shown, the theoretical model predicts only four frequencies, as indeed will any model of this sort which possesses an axis of symmetry‡. Thus, if all six bands observed by Schierkolk are fundamental frequencies characteristic of the molecule  $\text{NH}_3$ , then the molecule does not have an axial symmetry. It seems, however, possible that the faintest two of the six observed bands may be due to traces of impurities or perhaps to associated or ionized molecules. In view of this possibility the correlation will be carried out, choosing as fundamental bands the four strongest bands, namely, at  $10.7\mu$ ,  $6.14\mu$ ,  $2.97\mu$ , and  $2.22\mu$ . The theoretical frequencies contain three constants,  $K$ ,  $K'$ , and  $\frac{c}{a}$ , to determine which we shall use the three bands observed by both Coblentz and Schierkolk. Upon trying numerically

\* K. Schierkolk, *Zeit. f. Phys.* xxix. p. 277 (1924).

† In a recent note G. Hettner (*Zeit. f. Phys.* xxxi. p. 273, 1925) has pointed out that, if the bands at  $10.7\mu$  and  $6.14\mu$  be taken as fundamental, the remaining bands, both faint and strong, to a fair approximation fall near the positions of the higher harmonics of the two fundamentals. This may perhaps be only a coincidence, however, since the relative intensities as well as the exact positions of these "harmonic" bands seem to differ rather much from what might be expected from a molecule whose motion is nearly harmonic.

‡ One of the cases treated by F. Hund (*l. c.*) is that of the equilibrium of the molecule of ammonia, where he has shown that, if the electronic configuration about the nitrogen, originally central, is capable of a polarization induced by the hydrogen nuclei, the molecule in the normal state must have just the axial symmetrical form assumed here. In considering the vibrations of such a molecule he erroneously states that there will exist only three active frequencies, whereas, unless the particles all lie in the same plane, there must in general exist four. The table of harmonic and combination bands given by him may easily be changed to take account of this, however, by allowing the band at  $2.97\mu$  (calculated  $2\nu_2$ ) to become the fourth fundamental band.

all possible correlations it is found that only one leads to real values for constants, this leading to two solutions which lie quite close together. That is to say, within a certain range there may be a close correlation between three of the theoretical and experimental frequencies, and this correlation is considerably strengthened by finding that the fourth theoretical frequency lies very near to the fourth observed band. In the following table a set of values has been chosen for the constants which lies between the two solutions just mentioned with the view of slightly adjusting the values of the frequencies and also of the relative intensities. While this is rather arbitrary it can in no case make any great difference, since the functions change only by small amounts between the two solutions :

$$K = 27.8 \times 10^4$$

$$K' = 36.8 \times 10^4.$$

$$\frac{c}{a} = 0.255$$

	Frequency (Theo.).	Frequency (Obs.).	$\rho_i^2$ (Theo.).	$\rho_i^2$ (Obs.).
$\nu_1$ II .....	$1335 \times 10^{11}$	$1340 \times 10^{11}$	0.0076	0.12 —
$\nu_2$ II .....	282	281	0.40	0.95 —0.84
$\nu_3$ I .....	1009	1009	0.056	0.060—0.065
$\nu_4$ I .....	488	474	0.251	0.251—0.251

In computing the observed intensities, the *a priori* probabilities of the states  $\nu_3$  and  $\nu_4$  are assumed to be twice those of the states  $\nu_1$  and  $\nu_2$ , since the corresponding roots of the determinant  $\lambda_3$  and  $\lambda_4$  are double roots, whereas  $\lambda_1$  and  $\lambda_2$  are single. When two values of  $\rho_i^2$  (obs.) are given, the first is from the work of Schierkolk and the second from that of Oblentz, where the constants have been so chosen that all intensities agree at the band  $\nu_4$ , since here the experimental values seem most accurate.

While the theoretical and observed intensities do not check quite satisfactorily throughout the whole four bands, it is seen that, independently, for the bands corresponding to the same direction of vibration of the electric moment, that is  $\nu_1$  and  $\nu_2$  or  $\nu_3$  and  $\nu_4$ , there is a fairly good agreement. This result will not appear surprising in the light of the discussion at the conclusion of this paper, where it is shown that the change of the electric moment may depend not only upon the absolute value of the displacements of the particles, but also to some

extent upon the directions of their displacements. In the present case no two of the vibrations are exactly similar, but pairs of vibrations having the same direction of oscillation of the electric moment will obviously resemble each other more closely than pairs for which this direction is different.

In the present paper no attempt will be made to go into the fine structure of these bands, although one remark may be made concerning the separation of the temperature maxima of the envelope of the fine structure lines. According to Schierkolk the most probable frequency of rotation for the band at 281 is greater than that for the band at 474 by a factor of about  $\sqrt{2}$ . This is, qualitatively at least, in agreement with the predictions of the model, since the vibration  $\nu_2$  is parallel to the symmetry axis and hence its fine structure depends only upon the smaller moment of inertia C, whereas the fine structure of the vibration  $\nu_4$ , which is perpendicular to this axis, depends also upon the larger moment of inertia A. The ratio of A to C as given by the theoretical model is  $\frac{A}{C} = 1.51$ .

### § 5. *The Absolute Value of the Absorption of the Fundamental Bands.*

In the present section we shall consider the absolute absorption of a harmonic oscillator of frequency  $\nu_i$ , the amplitude of the oscillation of whose electric moment has the value  $\epsilon_i E_i$ . Equations (1) and (2) may be written as follows, where N is the number of molecules per unit volume in the normal state and the other symbols have their previous meanings:

$$A_0^i(h\nu_i) = \frac{8\pi h\nu_i^3 g_0}{c^2 N g_i} I_i, \quad \dots \quad (1')$$

where  $I_i = \int_0^\infty \alpha_{\nu_i} d\nu_i$ ,

$$A_0^i(h\nu_i) = \frac{1}{3}(2\pi)^4 \frac{\epsilon_i^2}{c^3} \nu_i^4 E_i^2. \quad \dots \quad (2')$$

For convenience we may consider  $E_i$  to be the amplitude of vibration of the nuclei and  $\epsilon_i$  their "effective" charge. Equating the last two relations and solving for  $\epsilon_i^2$ , we have

$$\epsilon_i^2 = \frac{3hcg_0}{2\pi^3 N \nu_i g_i E_i^2} I_i. \quad \dots \quad (3)$$

In the case of a diatomic molecule,

$$g_0 = g_i$$

and 
$$E_i^2 = \frac{h}{2\pi^2\mu\nu_i},$$

where  $\mu$  is the reduced mass of the nuclei.

Substituting \*,

$$\epsilon_i^2 = \frac{3\mu c}{\pi N} I_i. \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

In the more general case of a polyatomic molecule, equation (3) takes the form

$$\epsilon_i^2 = \frac{3cMg_0}{\pi NF_i^2 q_i} I_i, \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

where  $M$  is a function of the masses of the nuclei and  $F_i$  is the factor connecting the amplitude of the electric moment with the amplitude of the normal coordinate  $X_i$ .

An accurate determination of  $\epsilon_i$  by means of experimentally known values of  $I_i$  seems to be rather difficult, since, unfortunately, if the fine structure lines are narrow, much smaller than the slit width, the observed value of  $\alpha_{\nu_i}$  is less than its true value averaged over the region of the slit width. A study of the existing data seemed to show, however, that for the bands considered in this section the error introduced in  $I_i$  cannot be greater than that of a factor of 2, and hence that in  $\epsilon_i$  is not greater than that of a factor 1.4. In the following table the values of the integral of the absorption coefficient  $I_i$  are estimated only, since errors due to this cause will be of a lower order of magnitude. The action of the incident radiation will not appreciably disturb the temperature equilibrium of the gas, and for all the cases treated in the table,  $N$ , the number of molecules per c.c. in the normal state, has been taken equal to the total number of molecules present per c.c.

\* This formula might as well have been derived from the well-known relation that a linear oscillator absorbs an energy  $\frac{\epsilon^2\pi}{3\mu}$  per second, independent of its amplitude. The fact that the two derivations lead to the same result depends upon using for  $E_i$  the amplitude of vibration in the upper state.

Substance.	$\frac{M}{F_i^2 \times 1.65 \times 10^{-24}}$	$\frac{g_0}{g_i}$	$I_i \times 10^{-10}$	Observer.	$\frac{\epsilon_i}{4.77 \times 10^{-16}}$
HCl.....	0.973	1	71 60 52	E. v. Bahr* " " Burmeister ( <i>l. c.</i> )	0.075 0.068 0.064
					0.069
HBr.....	0.988	1	25 (?)	Burmeister	0.044 (?)
CO .....	6.86	1	27 32	Burmeister Coblentz ( <i>l. c.</i> )	0.123 0.133
					0.128
CO <sub>2</sub> ..... ( $\lambda = 14.66 \mu$ )	8.74	1	10.3 12.7	Coblentz Rubens and Aschkinass †.	0.085 0.094
					0.090
NH <sub>3</sub> ..... ( $\lambda = 6.14 \mu$ )	3.98	$\frac{1}{2}$	232 250	Coblentz Schierkolk ( <i>l. c.</i> )	0.192 0.200
					0.196
OH <sub>4</sub> ‡ .....	3.65	$\frac{1}{2}$	98	Coblentz	0.095
( $\lambda = 7.7 \mu$ )					

\* E. v. Bahr, *Verh. d. D. Phys. Ges.* xxi. p. 115 (1913).

† Rubens & Aschkinass, *Ann. d. Phys. u. Chem.* lxiv. p. 584 (1898).

‡ The values of  $\frac{M}{F_i^2}$  and  $\frac{g_0}{g_i}$  are taken from the author's paper on methane, mentioned in the introduction.

In the above table the values in the column  $\frac{\epsilon_i}{4.77 \times 10^{-16}}$  are equal to the square root of the ratio of the observed absorption to the absorption of an oscillating dipole of charge unity ( $4.77 \times 10^{-10}$ ) and reduced mass  $\frac{Mg_0}{F_i^2 g_i}$ . While it must always be remembered that  $\epsilon$  is only a measure of the amplitude of oscillation of the electric moment, it may be of convenience to think of the observed absorption as being produced by the molecule in question whose nuclei are centres of effective charges  $\epsilon_i$ . For the molecules CO<sub>2</sub>, NH<sub>3</sub> and CH<sub>4</sub>, the values given are to be associated with the C, N and C nuclei respectively, whereas the effective charge of each O, H and H nucleus is to be taken as  $\frac{1}{2}$ ,  $\frac{1}{2}$  and  $\frac{1}{4}$  of the table values respectively.

While, as has been mentioned, the values given for  $I_i$  are

only approximate and may be somewhat too small, due to the narrow character of the fine structure lines, it is seen from the table that the observed absorption is of quite another order of magnitude from that which might be expected from a molecule whose nuclei possessed effective charges of unity. Thus, for example, in the case of HCl, if the electronic configuration was centrally symmetrical about the chlorine nucleus throughout the motion, the absorption should be about 210 times greater than that actually observed. Such a result seems to show that the central symmetry of the electrons about the chlorine ion has been essentially disturbed by the presence of the hydrogen nucleus, in such a way as to greatly lower the effective charge of the latter.

For the molecule of methane there exists some independent evidence which is directly in accord with the low values of the effective charge found here, for, in the author's paper on the methane spectrum, it has been shown that in order to obtain any correlation between the observed fundamental bands and the normal frequencies of the theoretical model, it is necessary to assume that the repulsive force acting between the hydrogen nuclei is a very small fraction of the force that would exist if the hydrogen nuclei possessed effective charges of unity and the electronic configuration was centrally symmetrical about the carbon nucleus.

In the case of HCl it may be of interest to compute the electric moment in the normal state, identifying for the moment the value of  $\epsilon_i$  given in the table with the effective charge on the nuclei. The distance between the nuclei is known from the infra-red spectrum to be

$$d = 1.265 \times 10^{-8} \text{ cm.},$$

and hence the electric moment

$$\mu = 1.265 \times 0.069 \times 4.77 \times 10^{-18} = 0.42 \times 10^{-18}.$$

The value of the electric moment of HCl in the normal state has been found by Frivold and Hassel\* to be

$$\mu = 1.48 \times 10^{-18}$$

from dielectric constant measurements, under the assumption that the orientation of molecules is that given by classical theory. They state that if quantum theory assumptions are used as to the orientation, the value of  $\mu$  should be reduced by a factor of about  $\frac{1}{2}$ .

\* O. E. Frivold & O. Hassel, *Phys. Zeit.* xxiv. p. 82 (1923).



It seems, however, that it may be more correct to employ the random orientation of the classical theory in interpreting their data, since the experiments were carried out at atmospheric pressure, and it seems likely that the average number of impacts per second suffered by the molecules would be large enough to more or less destroy the effects of a space quantization.

Clearly no agreement could be claimed between the above values of  $\mu$  due to the nature of the problem, since the former is a measure of the absorption and depends upon the effect of a small displacement of the nuclei on the electric moment, whereas the latter represents the total electric moment of the charges in their equilibrium positions. In fact, the non-agreement of these values seems to make it certain that an accurate estimate of the absorption must be based not only upon the motion of the nuclei, but also upon the influence of this motion on the electronic configuration. The assumption as to the change of the electric moment made in §1 should accordingly be modified by saying that the change of the electric moment is proportional to the displacements of the particles relative to their centre of gravity, but that, in general, the proportionality factor may depend upon the directions of the displacements. This modification in the assumptions would have no effect upon the treatment of the absorption of diatomic molecules considered in §2, but might influence the results of the two succeeding sections to the extent that only a general agreement should be expected between the observed and calculated intensities of absorption.

I should like to take this opportunity to express my gratitude to Professor N. Bohr and Dr. H. Kramers, who have greatly aided the course of this paper both through their constant interest and through their many valuable suggestions. I also wish to express my appreciation of stipends from the International Education Board and from the University of Michigan, which have enabled me to carry on this work in Copenhagen.

Institute for Theoretical Physics,  
Copenhagen.  
June 9, 1925.

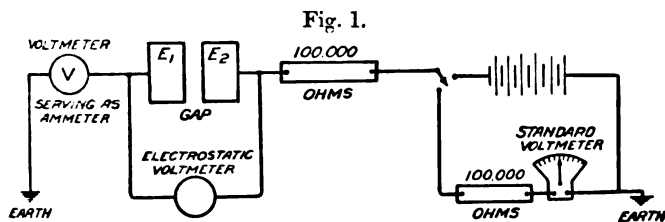
XIII. *The Relation between Temperature and Minimum Sparking Potential.* By E. F. BURTON, Ph.D., Professor of Physics, University of Toronto\*.

THE present investigation was undertaken to fill a gap in experimental work relating to the spark discharge in gases. The laws of spark discharge as related to variation of the gas, of pressure, of distance between electrodes, and of material in the electrodes have been determined by many workers†. Recently Meyer‡ and Wehrli§ have determined the effect of a magnetic field on the minimum sparking potential.

As for variation in temperature, the only direct references of which the writer is aware are the experiments of Whitehead|| and Ryan¶ on the variation of the dielectric strength of air with temperature. The former found that for a range from 6°C. to 41°C. the dielectric strength suffered a loss of 0.22 per cent. per degree rise in temperature.

*Apparatus.*

The lay-out of the apparatus is shown in fig. 1. The electrodes ( $E_1$ ,  $E_2$ ) were small solid cylinders of brass about 1 cm. in diameter, kept at a distance of about 4 mm.



apart inside a small quartz tube  $Q$  (see fig. 2). The electrodes were maintained in fixed position by means of the quartz nodules ( $n$ ,  $n$ ) and the quartz bars ( $B_1$ ,  $B_2$ ) pressing against the stout straight wires ( $w$ ,  $w$ ). The quartz tube containing the electrodes was fitted loosely into an outer glass tube ( $A$ ), to which glass leading tubes were sealed in

\* Communicated by the Author.

† See 'Conduction of Electricity through Gases,' Sir J. J. Thomson (Camb. Univ. Press), Chapt. xiii; F. M. Clark, Gen. Electric Review, xxviii. 3, p. 158, March 1925.

‡ E. Meyer, *Ann. d. Phys.* lviii. p. 297 (1919); lxvii. p. 1 (1922).

§ Max Wehrli, *Ann. d. Phys.* lxix. p. 285 (1922).

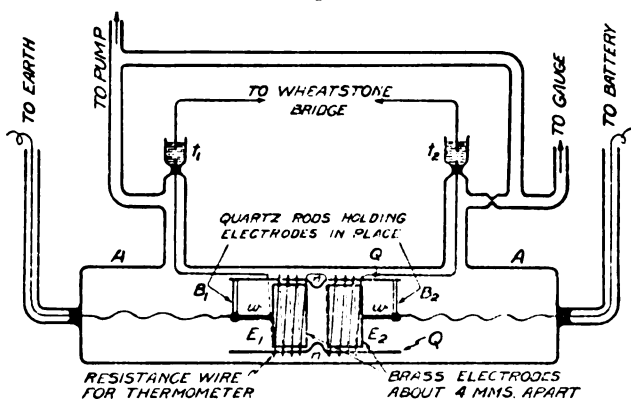
|| Whitehead, *Amer. Inst. Elec. Eng.*, xxix. 2, p. 1154 (1911).

¶ Ryan, *Amer. Inst. Elec. Eng.*, p. 101 (1904).

order that the metallic connexions with the electrodes could be insulated when the whole tube A was immersed in baths at different temperatures.

In order to find whether the actual discharge had an appreciable effect on the temperature of the spark enclosure, a coil of fine nickel-wire (number 34, .05 ohm per cm.) of about 21 ohms resistance was wound about the quartz tube and connected by means of the tubes,  $t_1, t_2$ , with a Wheatstone Bridge. It was found that there was no change of any importance in the resistance of the wire when the discharge was made to pass, under the conditions of this experiment, although the resistance varied quite regularly from 8 to 40 ohms when the temperature of the nickel wire was changed from  $-190^\circ \text{C.}$  to  $+200^\circ \text{C.}$  As this fact was

Fig. 2.



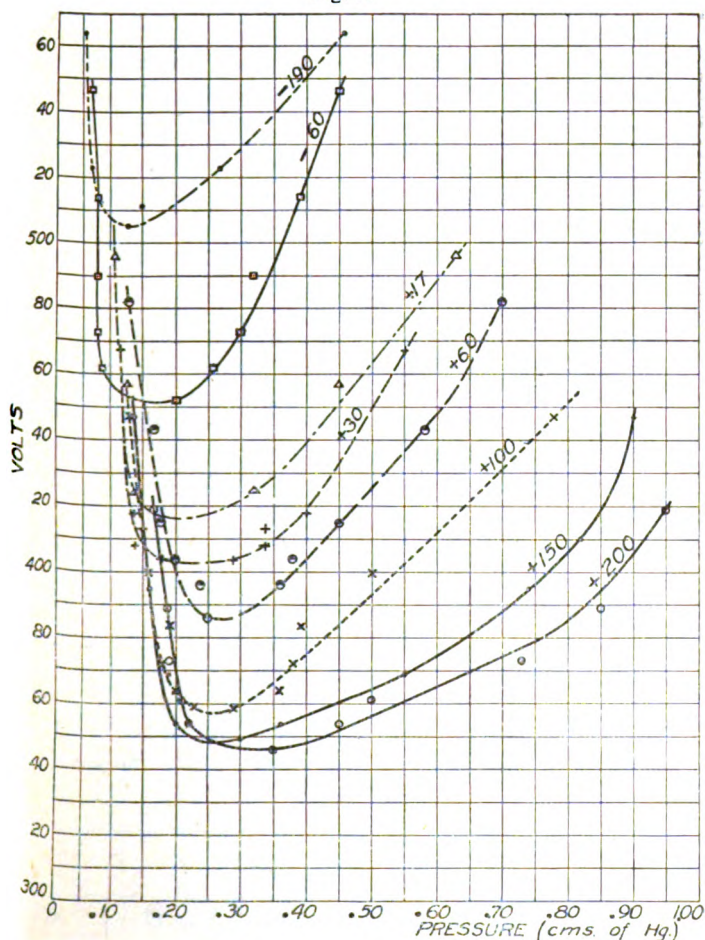
established beyond doubt, no further reference need be made to these temperature measurements. Since the nickel wire thermometer was calibrated before being sealed into the apparatus, two means of measuring the temperature of the electrodes was available, the nickel wire and an appropriate thermometer placed in the bath just outside the tube A.

In the final series of experiments the whole tube was surrounded by a copper rectangular bath ( $32 \text{ cm.} \times 8 \text{ cm.} \times 5 \text{ cm.}$ ), which was provided with an outer sheath of wire for electrical heating and an inner coil of copper tubing through which liquid air could be blown. For temperatures above zero, glycerine was placed in the bath; for those below zero, ether was used. The temperatures chosen for experiment were  $+200^\circ \text{C.}$ ,  $+150^\circ \text{C.}$ ,  $+100^\circ \text{C.}$ ,  $+60^\circ \text{C.}$ ,  $+30^\circ \text{C.}$ ,  $+10^\circ \text{C.}$ ,  $-60^\circ \text{C.}$ , and  $-190^\circ \text{C.}$

*Manipulation and Results.*

The method of determining the minimum sparking potential was that first used by Fierheller\*. A potential considerably higher than the minimum sparking potential was applied, gas pumped out very gradually and the

Fig. 3.



pressure noted at which the current was first indicated on the voltmeter (V), which served as a milliammeter; the pumping was then resumed and the pressure noticed at which the spark vanished. The applied potential was then

\* H. S. Fierheller, Trans. Roy. Soc. Canada, iii. p. 3 (1909).

reduced step by step and the above pressure readings repeated. The readings for different temperatures are given

TABLE I.  
Pressures at which Sparks Appear and Disappear at  
Different Voltages and Temperatures

200° C.			150° C.		
Press. in cm. Hg.			Press. in cm. Hg.		
Voltage.	Appear.	Disappear.	Voltage.	Appear.	Disappear.
419	·95	·17	447	·90	·14
389	·85	·19	410	·82	·15
373	·73	·19	395	·74	·16
361	·50	·21	369	·55	·19
354	·45	·22	354	·36	·20
346	·35	·35	350	·30	·30
100° C.			60° C.		
447	·78	·13	482	·70	·13
400	·50	·16	443	·58	·17
384	·39	·19	415	·45	·18
372	·38	·18	404	·38	·20
364	·36	·20	396	·36	·24
359	·29	·23	386	·25	·25
30° C.			17° C.		
467	·55	·12	496	·63	·11
418	·40	·14	457	·45	·13
413	·34	·15	424	·32	·14
408	·34	·14	410	No point.	
404	·29	·18			
-60° C.			-190° C.		
547	·45	·07	564	·46	·06
514	·39	·08	523	·27	·07
490	·32	·08	511	·15	·10
473	·30	·08	505	·13	·13
462	·26	·09			
452	·20	·20			

### *Temperature and Minimum Sparking Potential. 223*

in Table I. and illustrated by the curves in fig. 3. As the applied potential approaches the minimum looked for, both the pressures at which the spark appears and disappears and the corresponding currents (as given on V) approach to limiting values, so that the minimum can be very nicely determined.

The gas used was air freed from carbon dioxide and very carefully dried over large quantities of phosphorus pentoxide. Between readings sufficient of this dry air was admitted to the apparatus to give a pressure of four or five centimetres of mercury. Whenever the apparatus was left for any length of time, as, for example, overnight, it was exhausted to a few millimetres pressure.

One might expect to have considerable variation in the minimum potential even at a given temperature, due to possible changes in the electrodes with time. However, very consistent results were obtained, day after day, for the potential at the temperature of the room. In the final series of results which are recorded above, the bath was heated up to  $200^{\circ}\text{C}$ ., and a continuous series of experiments carried out down to temperature of  $-190^{\circ}\text{C}$ . without any great lapse of time; one may feel justified in saying that a variation in the electrode, merely through standing for a length of time, has been eliminated.

TABLE II.

Minimum Spark Potential and Temperature.

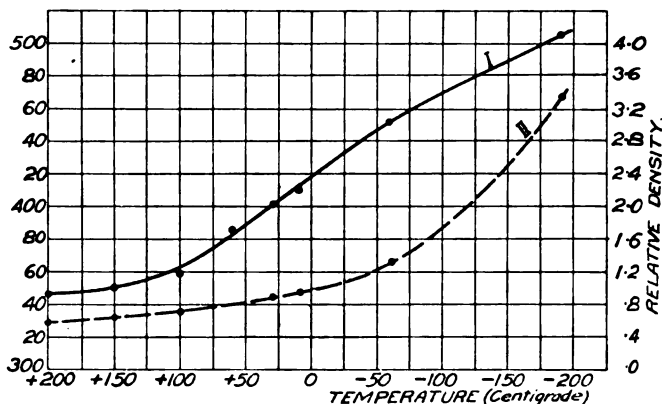
Temperature.	Relative Density.	Minimum Potential.
$200^{\circ}\text{C}$ .	·58	346
150	·64	350
100	·73	359
60	·82	386
30	·90	402
10	·96	410
-60	1·28	452
-190	3·37 (?)	505

Table II., which is illustrated by fig. 4 (curve I), gives the collected results of the minimum spark potentials and

## 224 *Relation between Temperature and Sparking Potential.*

temperatures. These results need no comment as far as the experimental facts are concerned.

Fig. 4.



As a result of early work on minimum spark potential, it has been shown that when the distance between the electrodes is varied as well as the pressure, the spark potential depends on the mass of gas per c.c. between the electrodes.

Consequently, the relative density of the air at different temperatures was calculated, the results being recorded in Table II. and illustrated by curve II in fig. 4. In calculating the density, the variations given by Charles' law were used; as shown by the experiments of Witkowski\*, the departure of air from the simple law from 100° C. to -145° C. is very small. The two curves of fig. 4 show a striking parallelism between the variation in the minimum potential of the spark discharge and the density.

I desire to express my thanks to Professor McLennan, Director of the Department of Physics, University of Toronto, for facilities offered in the cryogenic laboratory.

\* A. W. Witkowski, *Phil. Mag.* 5, xli. p. 288 (1896).

**XIV. the Non-Metallic Elements. Connexions between their Dielectric and other Physical Properties.—Part II.**

By G. L. ADDENBROOKE \*.

**I**N a previous communication (Phil. Mag. May 1924, p. 945) relations were shown between the dielectric properties of ten non-metallic elements and their thermal properties, and also with surface tension and capillarity. The close further connexion of the electrical with the corresponding optical properties was also alluded to in general terms.

The much more direct connexion of all these properties with electrical attraction than with the dielectric constant establishes a basis for comparing the electrical with the corresponding optical properties. Such comparisons are important, as it has long been recognized that the optical properties are closely related to atomic weight, valency, chemical action, and the deeper structural properties of matter, and thus the connexion of these with the purely electrical properties is made clearer. The connexion of the optical properties with the other physical properties dealt with in the first communication is also emphasized.

In the above communication the electrical properties of the elementary gases in the *liquid state* were dealt with. It is now proposed, as a commencement, to apply similar methods and reasoning to some of the elements in the *gaseous state*, as compared with the liquid and solid states.

TABLE VII.

Gases.

(For data, see tables, French Physical Society, 1913.)

Property.	Hydrogen.	Helium.	Oxygen.	Nitrogen.
K .....	1.000,273	1.000.140	1.000,543	1.000.581
N <sup>2</sup> .....	1.000,272	1.000,066	1.000,539	1.000,584

According to Avogadro's law, at the same pressure and temperature all these gases contain the same number of molecules. Since the molecules are a long distance apart, the action of the electric field must be directly on the molecules. It will be seen that K and N<sup>2</sup> are equal within probable errors of observation. The ordinary and atomic

\* Communicated by the Author.



dielectric constants and equivalents ( $K_m - 1$ ) are therefore the same for these gases.

As they stand, the figures are almost meaningless; taking the corresponding dielectric equivalents or ( $K_m - 1$ ) of these gases as defined in the above communication, they are closely in the proportion of:—

Helium .....	2	or 0.50
Hydrogen .....	4	„ 1.00
Oxygen .....	8	„ 2.00
Nitrogen.....	8.5	„ 2.12

The above relations were originally pointed out by Cuthbertson for the refractivities. For these refractivities  $N^2 = K$  within the probable errors of observation. For these small dielectric equivalents or refractivities the relative results will therefore be closely similar, whether the formula  $K - 1$

or  $\frac{K - 1}{K + 2}$  is used, or the equivalent optical formulæ  $N^2 - 1$

and  $\frac{N^2 - 1}{N^2 + 2}$ . Consequently the electrical results show that

for these gases the energy stored in an electrical field is closely proportional to the attraction, and the equal correspondences in the case of the optical results imply a similar connexion at the frequencies of light waves.

### *Liquid State.*

Consider next the liquid state of these elements when their molecules are brought six to ten times nearer each other than in the gaseous state, which is what occurs when the gases are liquified.

The data given in the table below for the densities, dielectric equivalents, and refractive indices<sup>2</sup> are those for the same temperature and density in the case of each element.

TABLE VIII.

Liquid State.

Element.	A.N.	A.W.	Density.	D.C.	$N^2$ .	$N^2 - 1$ .
Helium .....	2	4	0.15	—	—	—
Hydrogen .....	1	1	0.071	1.21	1.21	0.21
Nitrogen .....	7	14	0.88	1.43	1.43	0.43
Oxygen .....	8	16	1.25	1.465	1.480	0.48

The dielectric constants for this state again agree closely with the squares of the corresponding refractive indices. That for liquid hydrogen is taken from the refractive index, as it has not yet been measured directly. (See Science Abstracts 1200, 1914, and Phil. Mag. May 1924.)

*Comparison of Absolute Electrical Properties in Gaseous, Liquid, and Solid States.*

It has long been known that if the above gases are compressed, the values of the electric energy reversibly stored are given by the formula  $\frac{K-1}{D}$  within small limits, over a wide range of pressure : that is, the energy storage in an electric field is proportional to the number of molecules present in a given volume ; experimental results are available up to about 200 atmospheres.

But the densities and electric data are known for these gases in the liquid state as well as in the gaseous. We can therefore find how many times a centimetre of each element expands from the liquid to the gaseous state at 0° C. As then the number of molecules present in a given volume will be reduced in proportion to the expansion, we can compare the electrical action on a molecule in the gaseous state with that on a molecule when the molecules are aggregated in the liquid state, and when their distance from each other is reduced from six to ten times. The comparisons are made below.

TABLE IX.

Comparison of Dielectric Equivalents of Gases in Liquid and Gaseous States.

*Hydrogen Liquid.*—One gramme liquid, density 0.071, occupies 14.1 cm.<sup>3</sup> and 1 gramme gas at the atmospheric pressure and 0° C. fills 11,200 cm.<sup>3</sup> ; thus from liquid to gas at 0° C hydrogen expands :—

$$\frac{11,200}{14.1} = 975 \text{ times.}$$

K-1 of liquid hydrogen is 0.21 and 0.21 divided by 975=0.000263.

K-1 at atmospheric pressure and 0° C. is, by observation, 0.000273.

In the above it is assumed that  $K=N^2$ .

*Oxygen*.—From the liquid state at  $-180^{\circ}$  to A.P. at  $0^{\circ}$  C. oxygen expands 875 times.

$K-1=0.465$ , this divided by 875  $=0.000530$ .

The dielectric equivalent of the gas by observation at A.P. at  $0^{\circ}$  C.  $=0.000543$ .

Both the above are from direct observation.

*Nitrogen*.—The expansion of this gas is about 700 times from the liquid state at  $-200^{\circ}$  Density  $=0.88$ . Taking  $K-1$  as 0.45, this divided by 700 gives 0.000643.

The dielectric equivalent of the gas is, by observation, 0.000581.

In this case the data are a little more uncertain, but both the results are from direct observation.

### *Observations.*

In the above examples the densities of oxygen and nitrogen at about  $-190^{\circ}$  are employed, and for hydrogen,  $-252^{\circ}$ . From other data available it appears that by subtraction of more heat a further shrinkage takes place in these liquid gases as the temperature is lowered up to 10 per cent. or more by volume, but the dielectric constants are not yet available for these lower temperatures and greater densities.

Bringing the molecules still nearer would probably result in an increase of the dielectric equivalent beyond the corresponding increase in density; it may be assumed, however, that it would be small for the reasons given above.

If liquid gases of these increased densities were used the volume expansion would be correspondingly greater and thus the calculations above would not seriously be affected.

The above data, therefore, show that there is, to a close approximation, little change, not only in the relative values, but also in the atomic values of the energy stored and the corresponding attractions for a given number of atoms of these gases in an electric field of the same slope, for the gaseous and for the liquid state.

Apart from its intrinsic interest and as relating to elements so important and universal, this result supplies a basis for studying the atomic values of the actions in the other elements in the gaseous as compared with the liquid or solid states, since we can start from the same quantitative basis for both states.

Similar relations for the refractivities in the liquid as compared with the gaseous state were long ago pointed out by Living and Dewar, though their work seems to have been overlooked. As  $N^2$  is so close to the value of  $K$ ,

both for the liquid and gaseous states, it is now obvious that the above comparison applies equally to the refractivities as to the dielectric equivalents ( $K-1$ ).

These gases are only aggregated by extreme cold as well as pressure. Also (apart from helium), these gases have the lowest dielectric equivalents and attractions of any of the elements. It is, therefore, only to be expected that the interaction between their molecules in whatever state should be small.

### *Extension of above Results to other Elements.*

The dielectric constant of chlorine in the gaseous state is not known, nor are those of the rest of the elements we are dealing with in the state of vapour.

Owing to the long and beautiful work of Cuthbertson (Trans. Roy. Soc. 1902-1913), we have, however, the refractivities of all the elements dealt with, in the gaseous or the vapour states, reduced to  $0^\circ \text{C}$ . and 760 mm. pressure, as well as those of a number of others. We can, therefore,

get the values of  $N^2-1$  and  $\frac{N^2-1}{N^2+2}$  for all these elements in the gaseous state from Cuthbertson's data.

Suppose we write  $R$  for  $N^2-1$ , then  $\frac{N^2-1}{N^2+2}$  can be written  $\frac{R}{R+3}$ . Now, as  $R$  is exceedingly small for all the gaseous refractivities, the actual values of  $\frac{R}{R+3}$  will in all cases be one-third those of  $R$ , to a close approximation.

### *Discussion of Electrical and Optical Formulæ.*

The work of Boltzmann, and later of Thornton, has shown *experimentally* that in ordinary electric fields the formula  $\frac{K-1}{K+2}$  represents with closeness the relation of the attraction to energy stored, for values of  $K$  from 2 to 11, or for the values of the dielectric equivalent, or energy stored in the atoms of the dielectric itself ( $K-1$ ) of from 1 to 10. Below this value of  $K-1$  similar evidence could only be got from experiments on gases in the liquid state. The use of the formula for values of  $K-1$  of less than 1 rests therefore, so far, on a theoretical basis, although reasoning offers no suggestion that it should not fairly represent the same

relations for lower values than 1 of  $K-1$ , or of the energy stored in dielectrics themselves, apart from that stored in the field.

On the other hand, the formula  $\frac{N^2-1}{N^2+2}$  has been chiefly used by optical workers for small refractivities, where general experience has led to great reliance on it. For large ranges optical workers seem to have been chary in the past about drawing serious inferences from it; except in the cases in which  $K$  still equals  $N^2$ , there has apparently been no alternative method of co-ordination, or of experimentally checking the results, as there is in the corresponding electrical case.

The facts enumerated above, however, connect  $K$  and  $N^2$  very closely for low values, and, as pointed out above, values of  $K$  found by the attraction method, using the formula  $\frac{K-1}{K+2}$ , agree closely with those found by more ordinary electric methods over a larger range than we are dealing with here, while the connexion of  $K$  and  $N^2$  still remains intimate up to high values.

The implication is therefore very strong that as  $\frac{K-1}{K+2}$  represents attraction in the purely electrical case,  $\frac{N^2-1}{N^2+2}$  must be very closely connected with attraction also, for electromagnetic waves of the frequency of heat and light.

From what we know of the rapidity with which electric fields are propagated there is nothing to show that electric fields do not act similarly at the frequencies of electromagnetic waves of light.

Finally,  $N-1$  is the value measured by the refractometer or spectroscope. An electromagnetic wave has frequency and amplitude, and energy depending on the first two quantities. If it is taken that  $N-1$  depends on frequency and amplitude, the corresponding energy should be related at a given frequency to the square of the amplitude, and to  $N^2-1$ .

A close relation of this kind is the basis of the theories of Planck and Bohr.

It may therefore be taken that at any rate in cases where  $K$  and  $N^2$  are found to substantially agree, there is warrant for presuming a close connexion between the attractive forces at the frequencies of light and the energy stored, under the action of these forces, and that the connexion of

the two is fairly expressed by the formula  $\frac{N^2-1}{N^2+2}$ , as that between attraction and energy stored is by  $\frac{K-1}{K+2}$  for ordinary electric fields; the two formulæ being connected by the fact that  $K=N^2$  substantially for all the elements with which we are dealing.

*Application to Available Data.*

Below is a table in which are collected the observational data, both optical and electrical, for all the elements we are dealing with. The gaseous optical data have been kindly supplied by Mr. Cuthbertson. The only observations as regards these are that there is an absorption band in the iodine refractivity, and almost certainly a considerable reduction would result from a proper correction applied to the figure given. Such a correction is applied in the case of selenium, which was carefully investigated by R. W. Wood (see Phil. Mag. 1902).

TABLE X.  
Dielectric and Optical Properties of Elements.

Element.	Atomic Weight.	Squares of Refractive Index.		Dielectric Constants.		Densities.
		State of Elements.		State of Elements.		
		Gaseous.	Liquid or Solid.	Gaseous.	Liquid or Solid.	Liquid or Solid.
Helium .....	4	1·000,144	—	1·000,144	—	—
Hydrogen ...	1	1·000,272	1·21 D line	1·000,275	1·21 from N <sup>2</sup>	0·071
Nitrogen .....	14	1·000,584	1·45 b	1·000,581	1·45	0·88 at -20° 1·25 at -19°
Oxygen .....	16	1·000,539	1·46 b	1·000,543	1·47	
Chlorine .....	35·5	1·001,540	1·88 D line	—	1·97	1·5
Bromine .....	81	1·002,500	2·75 „	—	3·10	3·2
Iodine .....	127	1·003,840	3·70 „	—	4	4·66
Phosphorus..	31	1·002,430	4·14 „	—	3·85	1·84
Sulphur .....	32	1·002,220	4 „	—	4	2
Selenium .....	79	1·003,130	6·04 A line corrected	—	6·14	4·28
Diamond .....	12	1·000,750?	5·7 D line	—	5·5	3·5

Taking then the above data, these are analysed in Table XI.

TABLE XI.

Relative Values of Electrical and Optical Actions.

Element.	<i>a.</i>		<i>b.</i>		<i>c.</i>		<i>d.</i>	
	Gaseous or Vapour State.		Liquid or Solid States.		Gaseous or Vapour State.		Liquid or Solid State.	
	(1) $N_m^2 - 1$	(2) $K_m + 1$	(1) $N_m^2 - 1$	(2) $K_m - 1$	(1) $N_m^2 - 1$ $N_m^2 + 2$	(2) $K_m - 1$ $K_m + 2$	(1) $N_m^2 - 1$ $N_m^2 + 2$	(2) $K_m - 1$ $K_m + 1$
Helium .....	·50	—	—	—	·25	·25	—	—
Hydrogen ...	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0
Nitrogen .....	2·15	2·15	2·12	2·04	2·15	2·15	2·15	2·15
Oxygen .....	1·94	1·94	2·0	2·02	1·94	1·94	1·94	·94
Chlorine .....	5·57	Data wanting, but $K = N^2$ for liquid and solid states.	6·8	7·7	5·57	Data wanting, but $N = K^2$ in all cases for liquid or solid states.	5·6	6·1
Bromine .....	8·02		15·0	17·8	8·02		9·75	10·5
Iodine .....	14·2		25	27·7	14·2		12·4	13·3
Phosphorus...	8·55		17·3	10·2	8·55		10·9	10·1
Sulphur .....	7·7	Data wanting, but $K = N^2$ for liquid and solid states.	16·2	16·2	7·7	Data wanting, but $N = K^2$ in all cases for liquid or solid states.	10·1	10·1
Selenium.....	11·26		32·0	32·2	11·26		14·2	14·25
Carbon .....	—	Data wanting, but $K = N^2$ for liquid and solid states.	5·3	5·2	—	Data wanting, but $N = K^2$ in all cases for liquid or solid states.	4·6	4·5

The figures otherwise for the liquid and solid refractivities are left as they stand : in most cases any correction would be small. A somewhat larger correction is probably required for bromine and phosphorus, but since Cauchy's formula is inadequate, a special study of each of these elements on the lines of R. W. Wood's work on selenium would be required to get the true figures, and no such investigation seems to have been made in these cases.

The differences, however, are not likely to be great enough to alter the general conclusions which a further study of the relations reveals.

Beginning with the gaseous state, as already pointed out, according to Avogadro's law, all these gases will have equal numbers of molecules in a given volume. Consequently the data show the relative atomic as well as the absolute values. If then we take the value of hydrogen as unity and divide the other values by this, we shall get a set of relative atomic values as compared with that of hydrogen. This has been done for the columns *a* and *c* in Table XI. covering the gaseous state. It will be seen that the gaseous

electrical data for seven of the elements are wanting; but we have the facts that  $K=N^2$  for the three gases for which we have data, and that where data are wanting,  $K$  still equals  $N^2$  for the liquid and solid states of the same elements.

The columns of relative values for  $N_m^2-1$  for the liquid and solid states are calculated exactly as those for  $K_m-1$  in the first communication where the procedure was fully explained.

The columns for  $\frac{N_m^2-1}{N_m^2+2}$  are again calculated from those for  $N_m^2-1$  as before, for  $\frac{K_m-1}{K_m+2}$ . The columns for  $K_m-1$  and  $\frac{K_m-1}{K_m+2}$  for the liquid and solid states are taken from the first communication.

We now come to the relation of the gaseous values of both kinds to those for the liquid and solid states. It was shown above that the values for the same number of atoms for the elementary gases are substantially the same for both states, and that hydrogen expands 795 times between the liquid and gaseous states. If then the actual atomic values for the liquid and solid elements are all divided by 795, we get comparative tables of the atomic values for both states, and these will correspond to the relative values given in the table, the substantially constant values of hydrogen and oxygen for both states being taken in all cases as the basis.

### *Consideration of above Data.*

If now these four groups of tables are inspected it will be seen that:—

(1) *For the Gaseous State.*—The values of  $N^2-1$  are the same as those for  $K-1$  as far as they are available, within errors of observation. And this applies also to the similar values of  $\frac{N_m^2-1}{N_m^2+2}$  and if these are multiplied by 3, as explained above, the values all being very small.

(2) *For the Liquid and Solid States.*—Values of  $\frac{N_m^2-1}{N_m^2+2}$  and  $\frac{K_m-1}{K_m+2}$ . These values seem to be generally fractionally larger for the liquid and solid states than for the gaseous,



but otherwise they are again close to the values for the gaseous state.

(3) *For the Liquid and Solid States.*—Values of  $N_m^2 - 1$  and  $K_m - 1$ . When these two sets of relative values are compared they are again found to be very similar to each other. While, however, the values are again very similar to those in the other tables for the elementary gases, it will be noted that, as we come to elements with higher values of  $N^2$  and  $K$ , the proportionate values steadily increase as compared with the values of  $\frac{N_m^2 - 1}{N_m^2 + 2}$  and  $\frac{K_m - 1}{K_m + 2}$  for both states. Finally, for selenium (the element of highest atomic weight, attraction, and value for  $K$ ), the relative values are more than twice those for  $\frac{N_m^2 - 1}{N_m^2 + 2}$  and  $\frac{K_m - 1}{K_m + 2}$ . That is, the ratio of the value of energy stored to attraction is in the liquid state more than double that in the gaseous state. The atomic value for hydrogen, which is the same for both states, being taken as unity in both cases.

*Alternative method of establishing the above relations.*

The densities of all the above elements are known for the solid or liquid and for the gaseous states. In the latter state all will have the same number of molecules per cm.<sup>3</sup> at N. P. T. The volume contractions from the gaseous to the liquid or solid state can therefore be found.

These are entered in column (a) in the following table :—

TABLE XII.

	a.	b.	c.	d.
Element.	Times expansion Liquid or Solid to Vapour at N. T. P.	A ( $N^2 - 1$ ) Gaseous (a) as above.	Liquid or Solid ( $N^2 - 1$ ).	Values of (c) taking (b) as unity.
Hydrogen ...	975	·265	·273	1·04
Nitrogen .....	700	·41	·43	1·06
Oxygen .....	875	·48	·48	1·02
Chlorine .....	475	·73	·88	1·2
Bromine .....	448	1·03	1·75	1·72
Iodine .....	410	1·57	2·70	1·72
Phosphorus	6 0	1·60	3·14	1·96
Sulphur .....	700	1·55	3·0	1·94
Selenium.....	605	1·90	5·04	2·65

Column (b) contains the refractivity<sup>2</sup> multiplied by the

number of times the gas contracts to the liquid or solid state. The resulting values give the refractivity<sup>2</sup> supposing there were no change in the atomic refractivity<sup>2</sup> between the two states.

Column (c) gives the actual refractivity<sup>2</sup> ( $N^2 - 1$ ) found by observation for the liquid or solid state.

Column (d) gives the ratio of the gaseous atomic refractivity<sup>2</sup> on the above basis to that actually found for the liquid and solid states. It will be seen that for the three noble gases the differences are small, as already pointed out. As, however, the dielectric equivalents and refractivities of the elements increase, and presumably the attractions of their atoms for each other, the differences become greater and finally more than double. These differences rise with increasing atomic weight or number, and also with position in the periodic table. The only apparent cause is the difference in aggregation.

It is noteworthy that the increasing differences also correspond with increasing differences in viscosity or hardness.

For the three noble gases Maxwell's law is closely obeyed for both states. Assume that if the dielectric equivalents ( $K-1$ ) for the vapours of the rest of the elements were found they would also accord with Maxwell's relation to the already known refractivities, as seems highly probable. Then we should have Maxwell's law obeyed to a close approximation for all these elements for both states.

But the atomic values would be different in the above proportions for the two states. Consequently we should have the refractivity and the dielectric equivalent for these elements varying through a considerable range in close agreement with each other. In considering the constitution of non-metallic matter it seems equally important to ascertain if possible whether the above deduction is correct, or, if incorrect, what are the real relations.

Experimenters in the past have been deterred from attempting to obtain these dielectric constants for various reasons, but recent experience of the writer's with liquid bromine, specially purified and dried by Professor H. B. Baker, shows that this can be kept for several weeks in the presence of large platinum surfaces without any action taking place. Prof. Baker has also shown that chlorine gas, highly dried, will not unite with equally dried hydrogen, even in sunlight.

Pending such final verification, we have the evidence adduced above, which seems almost conclusive and which

shows that the property of occluding energy (reversibly) in a given electric field is only a constant under clearly defined circumstances. It is a pity a better descriptive phrase than "the dielectric constant" cannot be found for this important and fundamental property of matter, and for the even more direct quantity ( $K-1$ ), which I have ventured to call the dielectric equivalent, or the equivalent of the energy stored in the dielectric itself.

*The Real Nature of Faraday's "Specific Inductive Capacity," called more lately, "The Dielectric Constant."*

Briefly, the property of matter called at present "the dielectric constant" is really an unfortunate name for the proportional amount of energy stored between the electrodes of a condenser and the field, plus that stored in a dielectric filling the space between them, in terms of the former.

When the energy stored between the electrodes is deducted and that only considered which is stored reversibly in the dielectric itself, it is evidently dependent for the non-metallic elements on the following factors:—

(1) Position in the periodic table. That is on the form of the arrangement of the electrons round the nucleus of each of the atoms of the dielectric.

(2) On the charges of the nucleus and of the corresponding number of electrons surrounding it in each atom. That is, for the dielectric elements in any given columns in the periodic table,  $K-1$  increases with the atomic number and weight, apparently nearly directly.

(3) On the aggregation of the atoms. For a given aggregation of atoms it is greater the higher the atomic value of ( $K-1$ ) as defined above. Therefore, in gases having small attraction, the increase is small, but grows greater in elements where the atomic attractions are greater and the aggregations denser. The larger changes occur where atoms of higher atomic numbers condense from a gaseous to a liquid or solid state.

Using the broad lines of the modern view of the character of atomic structure, it is easy to form a fairly comprehensive picture mentally of what occurs to dielectric matter when placed in ordinary electric fields.

This is especially the case if the views of the nature of ordinary electric absorption, mentioned later, are also adopted.

We have then a useful background for considering what takes place in dielectrics when absorption is present in addition to the fundamental action, which should form a foundation on which to develop sound views of the construction of non-metallic matter.

*Supplementary Evidence.*

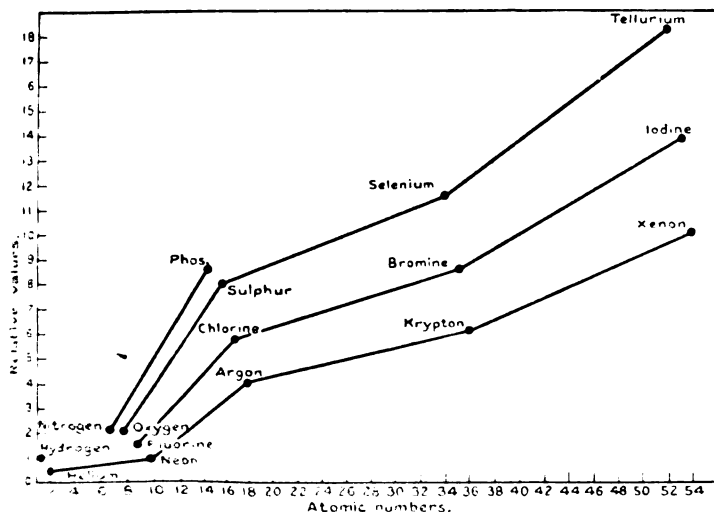
It has already been mentioned that Cuthbertson has found the gaseous refractivities for a number of other elements besides the ten or eleven with which we have been dealing. In view of the intimate connexion shown above between the purely electrical and the so-called optical properties of elements, for which we have the data for both properties, it is of interest to embody these further data in a diagram. This will include the data for the rare gases and also for gaseous tellurium and fluorine.

As these gaseous refractivities are very small,  $N-1$  will practically be equal to  $\frac{N^2-1}{2}$ , and to  $\frac{N^2-1}{N^2+2} \times \frac{3}{2}$  in all cases within the limits of accuracy to which we need go. Thus the relative values of all these properties can be represented by one set of relative values, if we take that of hydrogen as that of unity in each case.

*Gaseous State.*

Relative values of (2)  $N^2-1$  and (1)  $\frac{N^2-1}{N^2+2}$  (atomic), and thus presumably of

- (1) Electric attraction between molecules.
- (2) Electric storage capacity (atomic).



In the above diagram the abscissæ are atomic numbers and the ordinates the relative values of the above quantities, taking that of hydrogen as unity in all cases.

! The orderly way in which the various elements group themselves step by step in accordance with their position in the periodic table is very striking, as well as the very defined steps by which the properties progress from one group to the next higher. There is an evident sameness in the influence underlying the changes which occur between one group and the next. If we can connect these properties with the attractions due to electromagnetic waves impinging on the atoms and the corresponding amount of energy momentarily occluded in them, the connexions seem still more significant.

*Connexion with Ordinary Electrical Properties.*

Finally, it was shown above that the properties of the elementary gases, hydrogen, oxygen, and nitrogen, are substantially the same atomically in the liquid as well as in the gaseous state. If then the relative gaseous values are taken for  $N^2 - 1$  or the corresponding capacity for storing electric energy, and these relative values are multiplied by 975 for the elements below oxygen, it will be found that lower values result than the corresponding values for  $N^2 - 1$  and  $K - 1$  in the liquid or solid states. This again points to the view that the difference in capacity for storing electric energy in an electric field between the gaseous and liquid and solid states is due to aggregation of the atoms in the latter states. On the other hand, the values for the attractions (atomic) for both states accord fairly, so that while their values are only slightly modified by the state of aggregation of the atom, the energy stored due to this attraction is seriously increased with greater aggregation which also increases with atomic weight and position in the periodic table.

As regards boron, carbon, and silicon, reliable data for the gaseous state do not appear to exist at present, nor for boron and silicon in the solid state. If the electrical and optical data for these three elements could be found, the properties of the whole or of the non-metallic elements would be much better defined over an enormous range of wavelengths.

A moderate effort and financial expenditure, with some goodwill and organization, should enable all the above optical data to be checked and corrected for long waves, and the corresponding electrical data to be found. If such data were available, the results could hardly fail to help considerably in connecting our knowledge of the properties of atoms by themselves with those of the same atoms forming matter in the aggregate.

*Basis of above Comparisons.*

Although in these two communications the modern atomic theory has been freely used for purposes of illustration as undoubtedly giving much the most plausible explanations of the phenomena, it is worthy of note that none of the results depend on this theory.

Boltzmann showed experimentally, in 1873, that the ratio of the attraction of a dielectric to a metal sphere in an electric field could be expressed in terms of  $K-1$ , as  $\frac{(K-1)}{(K-1)+3}$ , or  $\frac{K-1}{K+2}$ , and his work was extended to a greater range of dielectrics by Thornton in 1908. Maxwell's relation was first put forward in 1865, and the corresponding optical formula  $\frac{N^2-1}{N^2+2}$  was advanced by the two Lorentz in 1890.

It is probable, therefore, that all the relations described above would have been discovered by this time, even if there had been no more detailed knowledge of the nature of the atom than there was in Maxwell's time.

*Effects of Aggregation on Atoms.*

Sir J. J. Thomson has for many years been pointing out that, in the case of a solution, the attraction (roughly defined by the dielectric constant) of the atoms of the solvent will loosen the bonds or lines of force binding the atoms of the molecules of the solute, and will exercise a powerful influence in causing the disruption of its molecules into ions.

But there is no difference in principle between the atoms of a solvent and a solute; they are equally made up of opposite electric charges. If, then, the atoms of a solvent act on those of a solute, as Sir J. J. Thomson has pointed out, it seems to follow that there must be a similar action between the atoms of the solvent itself tending to loosen the tension between the nuclei and surrounding electrons as compared with the same atoms in the gaseous state, thus making the whole aggregation more elastic.

Again, if an aggregation of atoms attract each other, and so loosen the bonds between the nuclei and their surrounding electrons, it seems to follow that if such an aggregation of atoms is put in an electric field some more of the lines which formerly anchored between the nuclei and the electrons will be diverted to the field, and so there will be a further

loosening or diversion of lines of force between the nuclei and electrons, and this may increase further the elasticity of of the whole aggregation and cause a very small but visible expansion.

Such an action might account for "Electrostriction." Quincke formed a leyden-jar of a thermometer bulb with the glass as the dielectric; on charging strongly the liquid in the stem sinks, that is, the glass expands.

If the above reasoning has solid basis, it seems possible to account in these ways for what is found to occur experimentally in good dielectrics in electric fields.

### *Nature of Absorption, Electrical and Optical.*

The so-called "resistance" of dielectrics is practically another name for absorption, and where the resistance is high, absorption is comparatively small. Where this latter is the case, measurements of capacity made with alternating currents of fair frequency give a close approximation of the true, or, as it has been called, the instantaneous or geometrical capacity, or the true capacity of the atoms of the dielectric itself when the capacity of the field itself is deducted.

Experiments on and investigation of the resistances of the dielectric elements in these communications led to the conclusion that for all the elements dealt with here the resistances were high enough to warrant the conclusion that the capacities and dielectric properties were sufficiently near the true ones to make legitimate the uses to which they have been put.

The value of the relationships found between the electrical and other physical properties of the elements would, however, be greatly enhanced if they could be followed up and applied to compounds formed from these different elements, but in these cases absorption may often be present.

If absorption in the general run of dielectrics at ordinary frequencies was part of the action of the field on the individual atoms of dielectrics, as has often been assumed in the past, the actions of ordinary electric fields on matter would, outside the best dielectrics, be very complicated and confusing.

Optical absorption, of course, rests on a different basis; this, which is generally of an atomic character, does not appear to come in until the frequencies of heat and light are approached.

The writer's experience, however, has led to the conclusion that ordinary electric absorption when seriously present is due, not to an action on the mass of the molecules of a

dielectric, but to action on small percentages of electrolytic impurities dissolved in the dielectric, which either wholly or in part are in an ionized state, as they would be in an electrolytic solution. (See *Journal Electrical Engineers*, February 1919, under "Institution Notes," also a long letter to 'Nature,' April 5th, 1924.)

The writer has recently found that similar views on absorption in almost similar terms were put forward by P. Curie in two lectures which he gave to the French Physical Society in 1892, as the result of work by his brother, J. Curie, and himself. They derived their conclusions chiefly from work on crystals. It is unfortunate that the lectures seem only to have been published in epitome. That such distinguished and far-seeing experimenters as the Curies should have arrived at almost precisely similar conclusions to the writer, on evidence derived from experiments of an entirely different character and by entirely different methods, encourages the writer to put forward more definitely the conclusions to which he has been led. Correct views of dielectric absorption are of great importance, not merely as a technical question, but in the study of physics and chemistry, and even in elucidating the nature and properties of matter itself.

These questions cannot be further discussed here, but it may be pointed out that what has been said above leads broadly to the view that there is no fundamental difference between what are called dielectrics and ordinary electrolytic solutions of all kinds; the apparent differences depend on the amount of ions present usually of a second substance, and the nature of the contact between the solvent and the electrodes and the liquidity or solidity of the matter through which the ions are diffused. In all these cases it would appear that the mass of matter forming the bulk of the substance is inert in electric fields, except for the attractions and reversible storage of energy taking place as described above. Electrolytic actions and the actions studied under the term "absorption" arise from the action of the field on the more or less free ions in electrolytes and more or less confined ions in dielectrics. It is to action on these ions and their consequent movements that changes of capacity with changes of frequency and temperature are due, as well as the dissipation of energy which is always found to occur concurrently, and which is usually studied as resistance or conductivity or dielectric hysteresis. Very small percentages of moisture or other electrolyte in dielectrics are found experimentally to have considerable effects.



Up to the end of last century there were no methods available for separating the capacity effects and dissipation of energy due to absorption in electric fields from the fundamental or instantaneous capacity, and much confusion of ideas resulted, and still exists.

By the use of the electrostatic wattmeter or by alternating bridge measurement, both of which methods have been greatly perfected during the last few years, it is now possible, at any rate in alternating fields, to separate the energy dissipated in dielectrics from that reversibly stored or from the capacity action. Further, by measurements over a range of frequencies, especially if very low frequencies are also used, change of capacity with change of frequency can also be measured. This change of capacity with change of frequency and the accompanying dissipation of energy, the writer's experiments show to be due to the presence of ions, the true instantaneous capacity being unaffected by change of frequency within ordinary limits. The very remarkable temperature coefficients of dielectrics are also found by experiments to be due to the presence of electrolytic ions and not to action on the mass of the molecules of dielectrics, the true temperature coefficients of which latter are, as those of the refractive index, always nominal.

In the above, and other ways, it is possible now to separate absorption effects, including both capacity and dissipation of energy, from the true basis capacity action to a fair approximation, and thus to arrive at a much closer idea of the real nature of the actions of dielectrics in electric fields and the real properties of matter.

Unfortunately, these methods have so far been applied to comparatively few dielectrics, but, from the writer's experience, if they were applied to the dielectrics in the long lists of dielectric constants given in the leading tables of physical constants, there would be considerable alteration in numbers of cases. This is the chief difficulty in pursuing the subject further at present. There is the same difficulty in applying much present data to problems in physical chemistry, as is now being done. False or incorrect inferences are being drawn, but if true data were available valuable light would be thrown on some of these problems.

Again, if the views expressed above are correct, we have a valuable means of studying absorption and electrolytic action by themselves.

It has only been possible to deal with the subject very cursorily, and it is difficult to avoid being misunderstood without writing at much greater length, but the object of

these two communications will have been attained if what has been said draws attention to the vast field for further experiment on recognized lines which is open in these directions, and which, if explored further, would certainly do much to extend and clarify our ideas of the physical actions which go to make up the properties of matter in the aggregate.

XV. *On an Experimental Investigation of the Applicability of Saint-Venant's Principle to the case of Frameworks having Redundant Bracing Members.* By Prof. A. J. SUTTON PIPPARD, *M.B.E., D.Sc., University College, Cardiff*, and G. H. W. CLIFFORD, *M.Sc.* \*

A RECENT paper † records an experimental verification of Castigliano's Principle of Least Work, and at the suggestion of Prof. Horace Lamb, F.R.S., the structural model and methods of strain measurement described therein were used to investigate the applicability to the case of redundant frameworks of Saint-Venant's Principle of the elastic equivalence of statically equipollent systems of load.

This principle states that the strains which are produced in a body by the application to a small portion of its surface of a system of forces statically equivalent to zero force and zero couple, are of negligible magnitude at distances which are large compared with the linear dimensions of the part ‡.

Saint-Venant gave no formal proof of this principle, which was enunciated with reference to elastic solids, but experimental evidence shows that the strains due to such a system become negligible at a comparatively short distance from the point of application of the forces §.

During the progress of an investigation into the distribution of stresses in the hull of a rigid airship ||, it appeared probable that the scope of the principle could be extended to the case of a framework having redundant bracing members, and a general demonstration of this was given by Mr. R. V. Southwell in a paper ¶ which also presented a physical basis for the principle in its usual form.

In the case of a simply stiff framework, *i. e.* one in which

\* Communicated by the Authors.

† *Phil. Mag.* l. (July 1925).

‡ A. E. H. Love, 'Mathematical Theory of Elasticity,' 3rd ed. p. 129.

§ Cp. G. F. C. Searle, 'Experimental Elasticity,' p. 31 *et seq.*

|| Aeronautical Research Committee R. & M. 800.

¶ *Phil. Mag.* xlv. (January 1923).

there are just sufficient bars to maintain the geometry of the structure, the internal stress distribution under any external load system is governed only by the configuration of the framework, and the stresses in a particular member may vary considerably under the action of load systems which are statically equivalent. It is therefore clear that the principle of Saint-Venant is not applicable to this class of framework ; it is only when the stress distribution becomes a function of the elastic properties of the framework that it can operate. This essential condition is fulfilled by a redundant structure, but since the degree of redundancy may range from a single member more than the number required for stiffness, to an infinite number in the extreme case of a solid body, it is clearly a matter of great importance to determine the effect of the number and disposition of redundancies upon the operation of the principle, and the experiments to be described were designed to contribute some information on these points.

By combining this principle with the principle of superposition, it follows that if any statically equivalent load systems be applied separately to a small portion of the surface, then the strains produced by these separate systems will tend towards the same values as the distance from the surface of application increases, and this modified form of the principle was found to be more convenient for experimental purposes than the original.

*Description of Experiments.*—The structure used in the experiments was the hexagonal braced tube with a  $\frac{7}{8}$  in. solid keel member, described and illustrated in the previous paper\*. This paper also describes the method of strain measurement.

The loads in the diagonal wire members only were measured, the longitudinal loads being obtained from these by resolution at the joints.

The framework was three bays in length, and a number of different statically equivalent load systems were applied to the bulkhead farthest from the wall and designated as bulkhead D.

Since it was desired to show if possible the effect of the disposition and number of redundancies, the experiments were divided into four sets as follows:—

*Set No. 1.*—All bulkheads unbraced ; all panels counterbraced.

*Set No. 2.*—Bulkhead D radially braced with 4 B.A. rods ; all panels counterbraced.

\* Phil. Mag. 1. (Experiment 3, p. 107).

Set No. 3.—Bulkheads C and D radially braced with 4 B.A. rods ; all panels counterbraced.

Set No. 4.—Bulkhead D radially braced with 4 B.A. rods ; compression counterbracing members omitted from all panels.

Fig. 1.

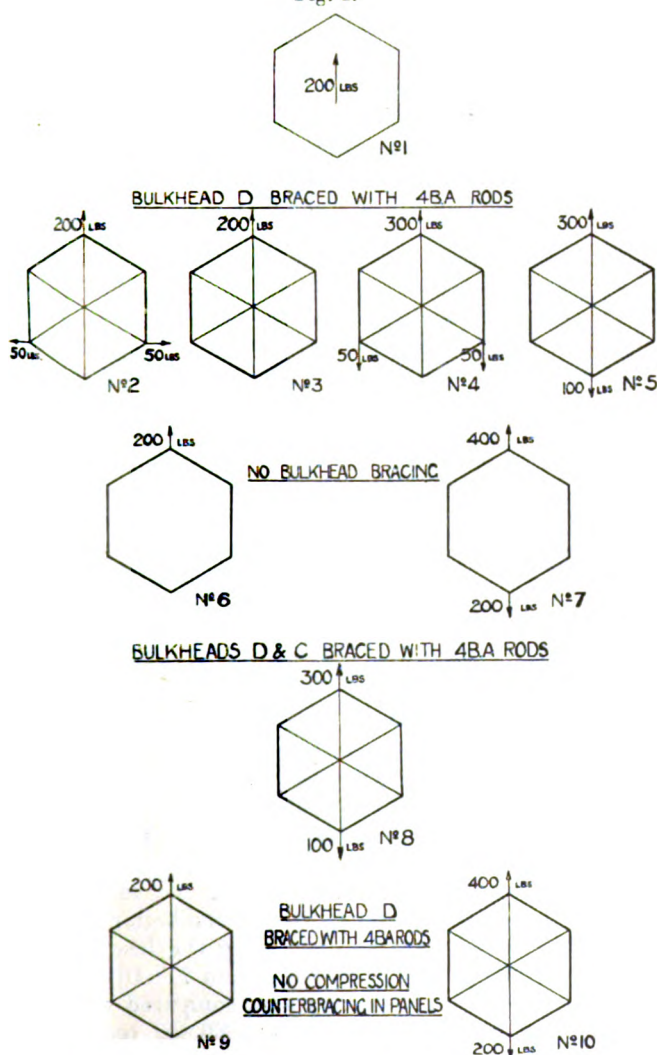


Diagram of loading and reference chart to experiments.

The scheme of the experiments and diagram of the load system is shown in fig. 1, the net shear being 200 lb. in each case.

A general theoretical solution for the stresses in a braced hexagonal tube, loaded at one end bulkhead and rigidly held at the other, has been obtained \* by assuming that the loaded bulkhead is rigid in its own plane, and that all transverse struts throughout the structure are inextensible. An extension of this solution to include the effect of the elasticity of the transverse struts shows this effect to be very small.

An identical stress distribution with that given on the assumption of a rigid bulkhead can be obtained if the bulkhead be considered to be unbraced, and the net shearing force to be obtained by a particular distribution of loads among the nodes of the transverse frame.

The stress distribution obtained from the general solution can thus be used as a theoretical datum for the first three sets of experiments, and for convenience of reference it is included in fig. 1 as No. 1.

Nos. 2-5 on the diagram show the load systems adopted in Set No. 2, these being the experiments actually carried out first. The greatest variations from the theoretical case were given by No. 5, and so for Set No. 1 the loadings No. 6 and No. 7 on the diagram were taken.

For Set No. 3 only one case, (No. 8 on the diagram), was measured for comparison with No. 1.

Nos. 9 and 10 illustrate the loadings adopted for the experiments of Set No. 4.

## EXPERIMENTAL RESULTS.

*Set No. 1. All bulkheads unbraced; all panels counterbraced.*

The loads in the wires as measured, and those in the longitudinals obtained from these are given in Table I. for load systems Nos. 6 and 7 on the chart.

It is evident at once that the load applied to the top joint of the structure as in load system No. 6, tends to stress mainly the members in the top panels, and in a length of three bays very little is transmitted to the bottom panels.

This effect is also seen by comparing the loads in the top panels (3-4) for the two cases Nos. 6 and 7. In load system No. 7 there is 400 lb. at the top joint compared with 200 lb. in load system No. 6, and the stresses in the top panels are approximately doubled. These are set out again in Table II. for easy reference.

\* Compare Aeronautical Research Committee R. & M. 800, Appendix V.

TABLE I.

Member.	Measured Loads.		Theoretical Loads.
	No. 6.	No. 7.	No. 1.
C <sub>1</sub> D <sub>1</sub> .....	Nil.	-228.4	33.6
C <sub>2</sub> D <sub>2</sub> .....	-2.8	85.6	17.6
C <sub>3</sub> D <sub>3</sub> .....	102.6	199.0	-11.6
C <sub>4</sub> D <sub>4</sub> .....	-211.6	-424.2	-50.6
C <sub>1</sub> D <sub>2</sub> .....	+3.6	-125.4	25.9
C <sub>2</sub> D <sub>1</sub> .....	Nil.	148.8	-21.9
C <sub>3</sub> D <sub>2</sub> .....	10.6	27.6	49.4
C <sub>4</sub> D <sub>3</sub> .....	Nil.	14.0	-49.0
C <sub>3</sub> D <sub>4</sub> .....	137.6	276.0	33.0
C <sub>4</sub> D <sub>2</sub> .....	-144.0	-286.0	-34.3
B <sub>1</sub> C <sub>1</sub> .....	+5.6	-578.4	101.2
B <sub>2</sub> C <sub>2</sub> .....	15.0	300.0	53.2
B <sub>3</sub> C <sub>3</sub> .....	263.4	530.0	-34.8
B <sub>4</sub> C <sub>4</sub> .....	-633.2	-1268.8	-152.0
B <sub>1</sub> C <sub>2</sub> .....	-5.2	-128.0	29.8
B <sub>2</sub> C <sub>1</sub> .....	Nil.	102.4	-18.0
B <sub>3</sub> C <sub>2</sub> .....	32.6	64.0	49.9
B <sub>4</sub> C <sub>3</sub> .....	-7.4	25.6	-48.4
B <sub>3</sub> C <sub>4</sub> .....	130.0	263.2	31.5
B <sub>4</sub> C <sub>2</sub> .....	-104.6	-204.4	-35.6
A <sub>1</sub> B <sub>1</sub> .....	-2.4	-918.8	168.9
A <sub>2</sub> B <sub>2</sub> .....	41.4	481.2	88.6
A <sub>3</sub> B <sub>3</sub> .....	378.8	812.0	-58.2
A <sub>4</sub> B <sub>4</sub> .....	-1001.2	-1996.2	-253.4
A <sub>1</sub> B <sub>2</sub> .....	-12.6	-132.6	33.8
A <sub>2</sub> B <sub>1</sub> .....	Nil.	93.6	-14.0
A <sub>3</sub> B <sub>2</sub> .....	62.4	104.0	50.4
A <sub>4</sub> B <sub>3</sub> .....	11.0	63.2	-48.1
A <sub>3</sub> B <sub>4</sub> .....	134.6	269.6	30.2
A <sub>4</sub> B <sub>3</sub> .....	-89.8	-181.6	-37.0

TABLE II.

Member.	Load System 6.		Load System 7.
	Load.	(Load) × 2.	Load.
C <sub>3</sub> D <sub>3</sub> .....	102.6	205.2	199.0
C <sub>4</sub> D <sub>4</sub> .....	-211.6	-423.2	-424.2
C <sub>3</sub> D <sub>4</sub> .....	137.6	275.2	276.0
C <sub>4</sub> D <sub>3</sub> .....	-144.0	-288	-286.0
B <sub>3</sub> C <sub>3</sub> .....	263.4	526.8	530.0
B <sub>4</sub> C <sub>4</sub> .....	-633.2	-1266.4	-1268.8
B <sub>3</sub> C <sub>4</sub> .....	130.0	260.0	263.2
B <sub>4</sub> C <sub>3</sub> .....	-104.6	-209.2	-204.4
A <sub>3</sub> B <sub>3</sub> .....	378.8	757.6	812.0*
A <sub>4</sub> B <sub>4</sub> .....	-1001.2	-2002.4	-1998.0
A <sub>3</sub> B <sub>4</sub> .....	134.6	269.2	268.0
A <sub>4</sub> B <sub>3</sub> .....	-89.8	-179.6	-181.6

\* This member shows a greater discrepancy, because it is the first to be affected appreciably by the variation in the stresses in the 2-3 panel wires.

On further comparison, the stresses in the members of the bay AB for the three load systems Nos. 6, 7, and 1, show very little tendency to converge to the same values.

It would appear, therefore, that in a framed tube in which all panels are redundantly braced, but in which there is no bracing in the plane of the applied load system, the operation of the Saint-Venant Principle, even if it exists, is a very slow process.

*Set No. 2. Bulkhead D radially braced with 4 B.A. rods ; all panels counterbraced.*

The various load systems applied in this case are shown in the diagram Nos. 2-5. Of these the stresses for No. 3 had

TABLE III.

Member.	Calculated Load. lb.	Measured Load. lb.				
	1.	2.	3.	4.	5.	
C <sub>1</sub> D <sub>1</sub> .....	33.6	35.1	32.5	36.3	21.6	
C <sub>2</sub> D <sub>2</sub> .....	17.6	18.0	19.0	15.1	27.3	
C <sub>3</sub> D <sub>3</sub> .....	-11.6	-12.2	-11.8	-9.2	-8.2	
C <sub>4</sub> D <sub>4</sub> .....	-50.6	-50.8	-52.0	-54.9	-63.4	
C <sub>1</sub> D <sub>2</sub> .....	25.9	26.0	24.7	25.8	14.5	
C <sub>2</sub> D <sub>1</sub> .....	-21.9	-22.8	-21.1	-23.6	-14.0	
C <sub>2</sub> D <sub>3</sub> .....	49.4	49.7	49.6	49.6	51.0	
C <sub>3</sub> D <sub>2</sub> .....	-49.0	-49.4	-49.4	-45.4	-50.0	
C <sub>3</sub> D <sub>4</sub> .....	33.0	33.0	33.8	35.7	41.2	
C <sub>4</sub> D <sub>3</sub> .....	-34.3	-33.8	-34.2	-37.6	-40.3	
B <sub>1</sub> C <sub>1</sub> .....	101.2	102.6	98.8	101.2	65.8	
B <sub>2</sub> C <sub>2</sub> .....	53.2	54.0	55.0	50.3	73.0	
B <sub>3</sub> C <sub>3</sub> .....	-34.8	-35.7	-33.8	-24.4	-22.7	
B <sub>4</sub> C <sub>4</sub> .....	-152.0	-149.4	-153.0	-165.8	-177.4	
B <sub>1</sub> C <sub>2</sub> .....	29.8	29.9	30.3	27.3	26.5	
B <sub>2</sub> C <sub>1</sub> .....	-18.0	-17.9	-18.3	-16.4	-14.2	
B <sub>2</sub> C <sub>3</sub> .....	49.9	49.2	49.2	50.1	50.0	
B <sub>3</sub> C <sub>2</sub> .....	-48.4	-49.9	-48.7	-47.1	-49.0	
B <sub>3</sub> C <sub>4</sub> .....	31.5	31.0	31.6	34.4	33.8	
B <sub>4</sub> C <sub>3</sub> .....	-35.6	-35.0	-36.3	-40.1	-40.0	
A <sub>1</sub> B <sub>1</sub> .....	168.9	170.0	166.6	161.0	123.4	
A <sub>2</sub> B <sub>2</sub> .....	88.6	91.0	89.7	88.7	113.2	
A <sub>3</sub> B <sub>3</sub> .....	-58.2	-60.7	-57.8	-40.5	-42.0	
A <sub>4</sub> B <sub>4</sub> .....	-253.4	-248.7	-255.0	-280.8	-283.8	
A <sub>1</sub> B <sub>2</sub> .....	33.8	33.4	33.9	33.4	33.8	
A <sub>2</sub> B <sub>1</sub> .....	-14.0	-13.9	-13.7	-11.6	-10.9	
A <sub>2</sub> B <sub>3</sub> .....	50.4	49.7	51.2	48.0	50.3	
A <sub>3</sub> B <sub>2</sub> .....	-48.1	-50.2	-48.2	-49.6	-50.2	
A <sub>3</sub> B <sub>4</sub> .....	30.2	29.5	30.6	34.6	29.2	
A <sub>4</sub> B <sub>3</sub> .....	-37.0	-36.1	-37.2	-39.8	-40.4	



already been obtained in the earlier experiments\*, but all the others entailed new measurements. The stresses as measured and those calculated for No. 1 are given in Table III.

To show the variation in the stresses more clearly, the differences from the theoretical case have been calculated and are given in Table IV.

TABLE IV.

Member.	No. 2.	No. 3.	No. 4.	No. 5.
$C_1D_1$ .....	1.5	-1.1	2.7	-12.0
$C_2D_2$ .....	0.4	1.4	-2.5	9.7
$C_3D_3$ .....	0.6	0.2	-2.4	-3.4
$C_1D_4$ .....	0.2	1.4	4.3	12.8
$C_1D_2$ .....	0.1	-1.2	-0.1	-11.4
$C_2D_1$ .....	0.9	-0.8	1.7	-7.9
$C_2D_3$ .....	0.3	0.2	0.2	1.6
$C_3D_2$ .....	0.4	0.4	-3.6	1.0
$C_3D_4$ .....	0	0.8	2.7	8.2
$C_1D_3$ .....	-0.5	-0.1	3.3	6.0
$B_1C_1$ .....	1.4	-2.4	0	-35.1
$B_1C_2$ .....	0.8	1.8	-2.9	19.8
$B_3C_1$ .....	0.9	-1.0	-10.4	-12.1
$B_1C_4$ .....	-2.6	1.0	13.8	25.4
$B_1C_3$ .....	0.1	0.5	-2.5	-3.3
$B_2C_1$ .....	-0.1	0.3	-1.6	-3.8
$B_2C_3$ .....	-0.7	-0.7	0.2	0.1
$B_3C_2$ .....	1.5	0.3	-1.3	0.6
$B_1C_4$ .....	-0.5	0.1	2.9	2.3
$B_4C_3$ .....	-0.6	0.7	4.5	4.4
$A_1B_1$ .....	1.1	-2.3	-7.9	-45.5
$A_1B_2$ .....	2.4	1.1	0.1	24.6
$A_2B_3$ .....	2.5	-0.4	-17.7	-16.2
$A_1B_4$ .....	-4.7	1.6	27.4	30.4
$A_1B_2$ .....	-0.4	0.1	-0.4	0
$A_2B_1$ .....	-0.1	-0.3	-2.4	-3.1
$A_2B_3$ .....	-0.7	0.8	-2.4	-0.1
$A_3B_2$ .....	2.1	0.1	1.5	2.1
$A_2B_4$ .....	-0.7	-0.2	4.4	-1.0
$A_4B_3$ .....	-0.9	0.2	2.8	3.4

In a discussion upon the accuracy of the experimental results in the first paper, it was stated that repeat readings on the wires could be made to within  $\pm 1$  lb., so that it may be assumed that any variation within these limits can be neglected.

With the load system No. 2 only two wires out of eighteen measured show variations outside these limits, and in the case of load system No. 3 only one out of the eighteen exceeds 1 lb. and this only by 0.2 lb.

\* Phil. Mag. l. (1925).



It may be assumed, therefore, that within the limits of experimental accuracy, the load systems Nos. 2 and 3 give stresses agreeing throughout with the theoretical case No. 1.

With the load system No. 4 the variations are larger, but corrections of  $\pm 1$  lb. to the readings have such a considerable effect that deductions from this case are inconclusive.

TABLE V.

Member.	Load.		Variation of No 5 from No. 1.	
	No. 1.	No. 5.	lb.	Per cent. of No. 1.
$C_1D_1$ .....	33.6	21.6	-12	-35.7
$B_1C_1$ .....	101.2	65.8	-35.4	-35.0
$A_1B_1$ .....	168.9	123.4	-45.5	-27.0
$C_2D_2$ .....	17.6	27.3	9.7	55.0
$B_2C_2$ .....	53.2	73.0	19.8	37.2
$A_2B_2$ .....	88.6	113.2	24.6	27.6
$C_3D_3$ .....	-11.6	-8.2	-3.4	-29.3
$B_3C_3$ .....	-34.8	-22.7	-12.1	-34.8
$A_3B_3$ .....	-58.2	-42.0	-16.2	-27.8
$C_4D_4$ .....	-50.6	-63.4	12.8	25.3
$B_4C_4$ .....	-152.0	-177.4	25.4	16.7
$A_4B_4$ .....	-253.4	-283.8	30.4	12.0
$C_1D_2$ ... ..	25.9	14.5	-11.4	-44.0
$B_1C_2$ .....	29.8	26.5	-3.3	-11.0
$A_1B_2$ .....	33.8	33.8	0	0
$C_2D_1$ .....	-21.9	-14.0	-7.9	-36.0
$B_2C_1$ .....	-18.0	-14.2	-3.8	-21.1
$A_2B_1$ .....	-14.0	-10.9	-3.1	-22.1
$C_2D_3$ .....	49.4	51.0	1.6	3.2
$B_2C_3$ .....	49.9	50.0	...	...
$A_2B_3$ .....	50.4	50.3	...	...
$C_3D_2$ .....	-49.0	-50.0	...	...
$B_3C_2$ .....	-48.4	-49.0	...	...
$A_3B_2$ .....	-48.1	-50.2	2.1	4.3
$C_3D_4$ .....	33.0	41.2	8.2	24.8
$B_3C_4$ .....	31.5	33.8	2.3	7.3
$A_3B_4$ .....	30.2	29.2	...	...
$C_4D_3$ .....	-34.3	-40.3	6.0	17.5
$B_4C_3$ .....	-35.6	-40.0	4.4	12.3
$A_4B_3$ .....	-37.0	-40.4	3.4	9.2

With load system No. 5, however, the variations from No. 1 are much more marked, and the figures obtained have therefore been selected for detailed analysis.

In Table V. the variation of the stresses from those due to load system No. 1 are given as percentages of the latter. The members are arranged in groups of three, each group consisting of the corresponding members in the three bays. Variations of 1 lb. or less are neglected.

It will be seen that there are ten groups of corresponding members, and in seven of these groups there is a progressive drop in the percentage variation of stress from the bay CD to the bay AB. In two of the remaining three groups, (the 3-3 and 2-1), the figure for the bay BC does not lie between those for the other bays, although the variation is less in AB than in CD. Corrections of less than 1 lb. to the readings of one member in each group would, however, cause these two groups to show a progressive drop.

The only remaining group (3-2) can similarly be adjusted by corrections of less than 1 lb. to the readings.

Hence, seven of the groups show a progressive diminution of percentage variation without any correction of the experimental results, while adjustments of the remaining three by amounts within the limits of experimental accuracy would cause these to show a similar progression. Of the experiments in this set, therefore, the stresses for Nos. 2 and 3 agree almost exactly with those for No. 1, while No. 5 shows that there is a distinct tendency towards the equalization of stresses when bracing is provided in the plane of the external load system.

*Set No. 3. Bulkheads C and D radially braced with 4 B.A. rods ; all panels counterbraced.*

Since in Set No. 2 the load system No. 5 gave the greatest variation from the theoretical case, the same loading was adopted for the present set of experiments, in which the two bulkheads C and D were radially braced.

The loads for this case are given in Table VI., together with the variation from those of No. 1 as before, variations of less than 1 lb. being neglected.

In this set of experiments the loads afford very definite evidence of the rapid equalization of stresses. In five out of the six wires in the CD bay the variation between the two systems of loading is considerable, but in the bay AB the variation has been reduced to negligible dimensions in every

TABLE VI.

Member.	Loads.		Variation from No. 1.	
	No. 1.	No. 8.	Actual.	Per cent. of No. 1.
C <sub>1</sub> D <sub>1</sub> .....	33.6	22.8	-10.8	-32.2
B <sub>1</sub> C <sub>1</sub> .....	101.2	84.2	-17.0	-16.8
A <sub>1</sub> B <sub>1</sub> .....	168.9	151.0	-17.9	-10.6
C <sub>2</sub> D <sub>2</sub> .....	17.6	16.5	-1.1	-6.2
B <sub>2</sub> C <sub>2</sub> .....	53.2	55.5	2.3	4.3
A <sub>2</sub> B <sub>2</sub> .....	88.6	90.3	1.7	1.9
C <sub>3</sub> D <sub>3</sub> .....	-11.6	+1.0	-12.6	-108.6
B <sub>3</sub> C <sub>3</sub> .....	-34.8	-4.2	-30.6	-88.0
A <sub>3</sub> B <sub>3</sub> .....	-58.2	-28.4	-29.8	-51.2
C <sub>4</sub> D <sub>4</sub> .....	-50.6	-75.7	25.1	49.5
B <sub>4</sub> C <sub>4</sub> .....	-152.0	-197.5	45.5	30.0
A <sub>4</sub> B <sub>4</sub> .....	-253.4	-297.7	44.3	17.5
C <sub>1</sub> D <sub>2</sub> .....	25.9	19.3	-6.6	-25.4
B <sub>1</sub> C <sub>2</sub> .....	29.8	30.3	...	...
A <sub>1</sub> B <sub>2</sub> .....	33.8	33.7	...	...
C <sub>2</sub> D <sub>1</sub> .....	-21.9	-14.8	-7.1	-32.4
B <sub>2</sub> C <sub>1</sub> .....	-18.0	-20.6	2.6	+14.4
A <sub>2</sub> B <sub>1</sub> .....	-14.0	-13.1	...	...
C <sub>2</sub> D <sub>3</sub> .....	49.4	47.8	-1.6	-3.2
B <sub>2</sub> C <sub>3</sub> .....	49.9	50.7	...	...
A <sub>2</sub> B <sub>3</sub> .....	50.4	50.9	...	...
C <sub>3</sub> D <sub>2</sub> .....	-49.0	-40.8	-8.2	-16.7
B <sub>3</sub> C <sub>2</sub> .....	-48.4	-48.1	...	...
A <sub>3</sub> B <sub>2</sub> .....	-48.1	-48.8	...	...
C <sub>3</sub> D <sub>4</sub> .....	33.0	49.2	16.2	49.1
B <sub>3</sub> D <sub>4</sub> .....	31.5	30.1	-1.4	-4.5
A <sub>3</sub> B <sub>4</sub> .....	30.2	29.5	...	...
C <sub>4</sub> D <sub>3</sub> .....	-34.3	-49.1	14.8	43.2
B <sub>4</sub> C <sub>3</sub> .....	-35.6	-35.6	...	...
A <sub>4</sub> B <sub>3</sub> .....	-37.0	-37.4	..	...

case, and even in the bay BC four of the six wires show negligible variation.

The introduction of an extra bulkhead bracing system has therefore caused the stress equalization to take place much more quickly than is indicated by the results of the experiments of Set No. 2.

*Set No. 4. Bulkhead D radially braced with 4 B.A. rods ; compression counterbracing members omitted from all panels.*

In this set of experiments the compressive counterbracing members in all panels were omitted, so that, apart from the D bulkhead bracing, there were no redundancies in the framework. The two load systems are shown in the diagram as Nos. 9 and 10, and Table VII. gives the stresses obtained for the two cases. The theoretical stress distribution which would be obtained with a rigid bulkhead, or alternatively for a special arrangement of the external load, had already been calculated \*, and the figures reduced to correspond to the altered net shear force are quoted in Table VII. for comparison with the experimental values.

TABLE VII.

Member.	Loads.		
	Theoretical.	No. 9.	No. 10.
C <sub>1</sub> D <sub>1</sub> .....	0	0	0
B <sub>1</sub> C <sub>1</sub> .....	78	78.4	73.6
A <sub>1</sub> B <sub>1</sub> .....	156	154.0	142.2
C <sub>2</sub> D <sub>2</sub> .....	-39	-39.2	-36.8
B <sub>2</sub> C <sub>2</sub> .....	-1.5	-1.0	0.3
A <sub>2</sub> B <sub>2</sub> .....	36	39.6	41.4
C <sub>3</sub> D <sub>3</sub> .....	-76.5	-76.0	-71.4
B <sub>3</sub> C <sub>3</sub> .....	-105.0	-104.0	-87.9
A <sub>3</sub> B <sub>3</sub> .....	-133.5	-133.7	-111.1
C <sub>4</sub> D <sub>4</sub> .....	-96	-102.2	-121.6
B <sub>4</sub> C <sub>4</sub> .....	-192	-195.4	-227.2
A <sub>4</sub> B <sub>4</sub> .....	-283	-294.2	-330.6
C <sub>1</sub> D <sub>2</sub> .....	50.5	51.0	47.8
B <sub>1</sub> C <sub>2</sub> .....	50.5	49.2	44.6
A <sub>1</sub> B <sub>2</sub> .....	50.5	50.0	47.0
C <sub>2</sub> D <sub>3</sub> .....	99.5	98.8	92.8
B <sub>2</sub> C <sub>3</sub> .....	99.5	102.8	100.4
A <sub>2</sub> B <sub>3</sub> .....	99.5	99.2	98.8
C <sub>3</sub> D <sub>4</sub> .....	62.5	66.4	79.0
B <sub>3</sub> C <sub>4</sub> .....	62.5	60.6	68.6
A <sub>3</sub> B <sub>4</sub> .....	62.5	64.4	67.2

\* Aeronautical Research Committee R. & M. 971, Table I.

It will be noticed that the stresses in the three cases of this set are in reasonably good agreement in spite of the redundancies being confined to the loaded bulkhead. The tube was insufficiently long to allow definite conclusions to be drawn as to the applicability of the Principle of Saint-Venant to this case, but comparing the results obtained with those of Set No. 1, where all the redundancies were in the panel bracing, it is evident that redundant bracing when in the plane of the bulkhead is far more efficient than when placed in the panels, in conducing to an equalization of stresses.

These two conditions of the framework would appear to bear some analogy to the cases of a solid rod and a thin tube respectively, and it might be a matter of some interest and importance to investigate such cases to determine the distances required for strain equalization.

#### CONCLUSION.

The experiments lead to the following general conclusions:—

1. The Principle of Saint-Venant can be applied to the case of a redundant framework.

2. The operation of the principle is very slow if planes parallel to the loading plane are unbraced, even when the framework exhibits a high degree of redundancy in other planes.

3. If the plane of loading is braced, the tendency towards the equalization of strains is pronounced, and the distance required for the variation of strains to become negligible is dependent to a marked extent upon the efficiency of the bracing in this, and parallel planes.

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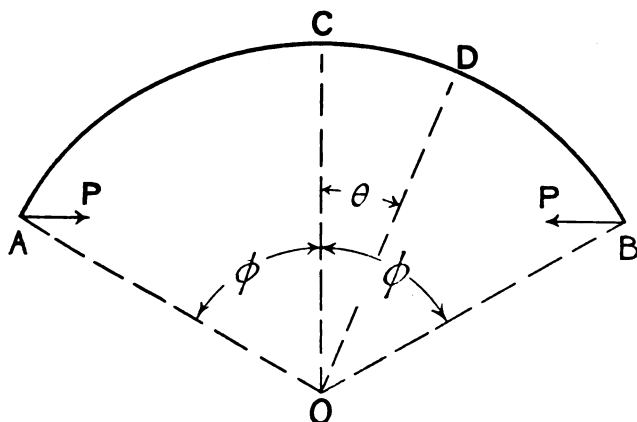
XVI. *On the Effect of Curved Members upon the Elastic Properties of a Framework.* By Professor A. J. SUTTON PIPPAED, M.B.E., D.Sc. University College, Cardiff\*.

THE elastic properties of a braced framework will govern the amount of its deformation under the action of external loads and also, in the case of a redundant frame, the distribution of internal stresses. Calculations of nodal displacements and stress analysis require, therefore, the introduction of this factor, and this may be conveniently done by the application of strain-energy methods†.

\* Communicated by the Author.

† Cp. Phil. Mag. vol. xlv. p. 194 (Jan. 1923).

In general, the component bars of a framework are straight, but in some cases, *e. g.*, in mediæval roof trusses, curved members occur, and these affect the elastic properties of the frame, and consequently its stiffness and stress distribution, to a considerable degree.



The present note indicates a general method for determining the effect of such members and for reducing frameworks containing them to cases in which standard methods of analysis may be used. The case of members curved to a circular arc is alone considered: this is the shape commonly found, but the method is readily adaptable to any other curve.

Let A and B be two nodes of a framework connected by a circular arc of radius R, and subtending an angle  $2\phi$  at the centre. If the frame is pin-jointed, any force transmitted between A and B must act along the line AB. Let P be such a force.

Then if  $\Delta$  is the amount by which the distance AB is shortened under the action of P,

$$\Delta = \frac{dU}{dP}, \quad \dots \dots \dots (1)$$

where U is the strain-energy of the bar.

If I is the moment of inertia of the cross-section of the bar,

A is the cross-sectional area of the bar ;

E is the modulus of elasticity of the material ;

N is the modulus of rigidity of the material.

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Then at any point D on the arc where  $\angle COD = \theta$  the resultant actions are :

an axial compression  $= P \cos \theta$  ;

a radial shear  $= P \sin \theta$  ;

a bending moment  $= PR (\cos \theta - \cos \phi)$  ;

and the total strain-energy of the bar is

$$U = \frac{P^2 R}{AE} \int_0^\phi \cos^2 \theta \cdot d\theta + \frac{P^2 R^3}{EI} \int_0^\phi (\cos \theta - \cos \phi)^2 \cdot d\theta \\ + \frac{P^2 R}{AN} \int_0^\phi \sin^2 \theta \cdot d\theta, \quad \dots (2)$$

where the first and second terms are the components due to axial load and bending respectively, and the third term is an approximation to the unimportant component due to shear.

Differentiating and evaluating, and giving N the value  $\frac{2}{3} E$ , we obtain

$$\Delta = \frac{PR}{AE} \left[ \frac{7\phi}{2} - \frac{3 \sin 2\phi}{4} + \frac{R^2}{k^2} \left( 2\phi - \frac{3 \sin 2\phi}{2} + \phi \cos 2\phi \right) \right], \quad \dots (3)$$

where  $k$  is the radius of gyration of the cross-section.

If the curved bar were replaced by a straight member of the same cross-sectional dimensions, but with such a value of  $E$  that  $\Delta$  remained the same, the elastic properties of the frame would be unaltered.

Let  $E'$  be the modulus of elasticity of such a member. Then, under the action of  $P$ , its alteration in length would be  $\frac{2PR \sin \phi}{AE'}$ , and for this to be equal to  $\Delta$  we must have

$$E' = E \left[ \frac{2 \sin \phi}{\frac{7\phi}{2} - \frac{3 \sin 2\phi}{4} + \frac{R^2}{k^2} \left( 2\phi - \frac{3 \sin 2\phi}{2} + \phi \cos 2\phi \right)} \right]. \quad \dots (4)$$

Any framework containing curved members can thus be simplified by replacing all such members by straight bars of the same cross-sections as the originals, but with modified values of  $E$  as given by equation (4). Such a simplified frame will be elastically equivalent to the original, and the usual methods for calculating deflexions and stresses can be employed.

The formula of equation (4) was verified by cutting two circular arc members from steel plate and experimentally

obtaining their load-compression curves. These curves were linear up to the yield-point, and the slopes gave the values of  $E'$ . The value of  $E$  for the material was found experimentally in the usual way. The results of the tests are given in the following table :—

Experiment.	Radius of arc.		Thick-ness.	$2\phi$ .	E.	E'/E.		
	In-ternal.	Ex-ternal.				Experi-mental.	Calcu-lated.	Error.
No.	inch.	inch.	inch.	degrees.	lb./sq. in.			%
1 .....	4.984	5.982	.727	180	26,960,000	.00346	.00348	0.58
2 .....	4.984	5.982	.727	120	26,960,000	.0164	.0171	4.1

These results show satisfactory confirmation of equation (4). Experimental difficulties in No. 2 which were absent in No. 1 account for the higher percentage error.

The method outlined in this note has been applied to the analysis of stresses in certain roof trusses, including the Westminster Hall roof, for the Building Research Station of the Department of Scientific and Industrial Research, the results being contained in a paper to be published shortly\*.

XVII. *Dimensional Analysis viewed from the Standpoint of the Theory of Similitudes.* By Mrs. T. EHRENFEST-AFANASSJEW, *Leiden (Holland)* †.

**T**HERE seems to be very little lacking at present toward freeing so-called "dimensional analysis" ‡ from all the mysticism which still clings to it, in spite of the great interest many physicists take in it. In this respect I am

\* "The Determination of Primary Stresses in Roof Trusses, with special reference to the case of curved members," by A. J. S. Pippard and W. H. Glanville.

† Communicated by Prof. Dr. P. Ehrenfest.

‡ This quite practical designation is given by P. W. Bridgman in his book 'Dimensional Analysis,' New Haven, Yale University Press, 1922. In it are discussed many typical examples of the customary use of dimensional analysis; the difficulties which arrest attempts to give dimensional analysis a theoretical basis also are given prominence in the introduction. As I see it, soundness will not be attained unless the standpoint of the theory of similitudes is assumed basically.





If we interpret equation (a) as the elastic oscillation equation, (b) as the Newtonian gravitation equation, and (c) as the "angle equation" (relationship between the central angle  $f$ , length of arc  $s$ , and radius  $r$ ),  $k$  will appear in all three equations as a coefficient which depends on the choice of units.

Of course, an advocate of dimensional analysis would immediately find a reason for giving dimensions to the coefficient  $k$  in equation (a):  $k$  is not simply a coefficient but a "physical constant"; that is, a variable quantity, which differs from one material to the next.

But how about equation (b)? Perhaps here, too, one would want to furnish an excuse: granted that we find in the entire real world only one kind of gravitating material, and that therefore  $k$  is a "universal constant" (in contrast to the various kinds of rubber which exert force according to equation (a)), there are other *conceivable* worlds in which  $k$  (with the same choice of units for all the other quantities) would have another numerical value.

But we still have equation (c); it is clear that in it the coefficient  $k$  has the dimension of an angle. And yet here neither of the two arguments presented above is valid, and it is therefore impossible to establish the thesis: "in an equation in which all physical quantities are explicitly given the coefficients are dimensionless."

What else is meant by the expression: "there are other conceivable worlds"? Let us compare in this respect examples (b) and (c): we may indeed think of worlds in which the relation between the central angle, radius, and length of arc of a circle is in general different from that in our world\*, but we cannot conceive of another Euclidean world — a world in which equation (c) holds, — in which  $k$  would have another numerical value; our intuition tells us directly that this is impossible. Our intuition relative to gravitational force, on the contrary, is very incomplete; we may write on paper a gravitation equation with a different coefficient  $k$ , and there is nothing to tell us whether such a formula still has any physical meaning. Thus the pretence

\* Thus, for instance, in a world in which the Riemannian geometry were valid, eq. (c) would be replaced by the following:

$$\phi = k \frac{s}{\sin \frac{r}{a}},$$

where  $a$  is the radius of curvature of the space, and  $r$  the radius of the circle.

that the gravitational constant is not a "coefficient" but a "variable quantity" remains undisputed. But when we have taken account of example (c), this pretence will no longer serve for establishing the presumed homogeneity of all physical equations. If nature can allow one non-homogeneous relationship between distinct quantities, as exists in eq. (c), what will give us a guarantee that there is not an abundance of other quantities which are also related to each other in non-homogeneous equations? \*

If therefore we know nothing else about an equation between certain variables,  $x_1, x_2, \dots, x_m$  except that it exists and that it involves no variables other than these, there exists the possibility that if all these variables were given in it explicitly, it might still involve dimensional coefficients (and that it could not be brought to a homogeneous form by any transformations). In this case, one would obtain a spurious form for it according to the method of dimensional analysis †.

§ 2. Nevertheless, there is the question, whether dimensional analysis may not after all be used with success in cases where we have definite grounds for assuming that the equation sought is certainly homogeneous. To this it is necessary to reply with two remarks: first, that these grounds may still be found illusory; second, that it is easy in the application of dimensional analysis to introduce ambiguities in the solution, which—as we shall see—may be diminished if the "theory of similitudes" is used instead of dimensional analysis. The former is so related to the latter in its method of calculating as to be mistaken for it frequently; however, it rests upon other, quite definite

\* And, if we do not want to enter uncontrollable discussions about other conceivable worlds, but look upon all coefficients which keep their values unchanged (as far as we are able to judge) as universal constants, an example occurs immediately in the gravitational equation. Presumably Planck's constant  $h$ , too, will figure in such a non-homogeneous, still unknown, fundamental equation.

† One might perhaps be inclined to desire a system, other than the C.G.S. system of dimensions, in which all coefficients of all physical equations were indeed dimensionless (the gravitation equation for instance becomes homogeneous, if one chooses a dimension-system—in adaptation to the same equation—so that mass involves the dimension  $[L^3T^{-2}]$ ). But eq. (c) directly offers an example of equations which cannot be made homogeneous by any change in the system of dimensions. Besides, it is clear that in general if the number of dimensional universal constants were to be more than two, the problem would already be over-determinate, for each "removal of dimensions" from a coefficient means a decrease in the number of fundamental variables (i. e., of variables whose units may be changed with entire freedom).

principles of pure mathematics, and can yield other results. Above all, its application is independent of the possibility that the equation sought may have dimensional coefficients. To be sure, it requires more data than dimensional analysis, but this is quite natural for a method which often gives more definite results, and never erroneous ones.

### METHOD OF SIMILITUDES.

§ 3. The method of similitudes starts with "*fundamental equations*," of which the desired equation is a consequence.

Let us assume that we know the complete system of fundamental equations of a problem :

$$\left. \begin{aligned} f_1(x_1, x_2, \dots, x_n) &= 0, \\ &\dots \dots \dots \\ f_k(x_1, x_2, \dots, x_n) &= 0. \end{aligned} \right\} \dots \dots \dots (1)$$

We will assume that this system "permits certain transformations." That is, if we introduce instead of the quantities  $x_1, x_2, \dots, x_n$  other quantities according to certain "*equations of transformation*":

$$\left. \begin{aligned} x_1 &= \phi_1(x'_1, x'_2, \dots, x'_n), \\ &\dots \dots \dots \\ x_n &= \phi_n(x'_1, x'_2, \dots, x'_n), \end{aligned} \right\} \dots \dots \dots (2)$$

we shall have exactly the same equations in the new variables:

$$\left. \begin{aligned} f_1(x'_1, x'_2, \dots, x'_n) &= 0, \\ &\dots \dots \dots \\ f_k(x'_1, x'_2, \dots, x'_n) &= 0. \end{aligned} \right\}$$

Obviously, every derived equation will also be invariant in undergoing transformations according to (2).

Suppose we look for a relation

$$\Phi(x_1, x_2, \dots, x_m) = 0 \quad \dots \dots \dots (3)$$

between a group of variables  $x_1, x_2, \dots, x_m$ ,  $m \leq n$ , which may be a consequence of equations (1). Suppose we succeed in setting up the most general form of invariant relations between the variables  $x_1, \dots, x$ . Then equation (3), if in general it exists, will obviously appear as a special case of this most general form.

Now a given system of equations (1) may admit, in

general, various kinds of transformations \*. We shall choose as "trial-transformations" for our purpose those for which the most general form of relations remaining invariant, as mentioned above, is especially easy to set up.

One such convenient kind of transformations constitutes the "similitude transformations" †. They are represented by

$$\left. \begin{aligned} x_1 &= \xi_1 x_1', \\ x_2 &= \xi_2 x_2', \\ &\dots \dots \dots \\ x_n &= \xi_n x_n', \end{aligned} \right\} \dots \dots \dots (2^*)$$

where  $\xi_1, \xi_2, \dots \xi_n$  are any fixed numbers (transition-factors).

It is clear that no equation between  $x_1, x_2, \dots x_n$  will permit this transformation if each number  $\xi_i$  is chosen quite independent of the others; since the fundamental equations remain invariant, there must exist certain relations of the transition-factors:

$$\left. \begin{aligned} \xi_{r+1} &= \psi_1(\xi_1, \dots \xi_r), \\ \xi_{r+2} &= \psi_2(\xi_1, \dots \xi_r), \\ &\dots \dots \dots \\ \xi_{r+l} &= \psi_l(\xi_1, \dots \xi_r), \end{aligned} \right\} \dots \dots \dots (3)$$

\* For instance, the system of equations

$$\begin{aligned} \frac{x^2}{z} + y^2 z &= \sin y^2 z, \\ a x^2 &= \frac{b}{y^2}, \end{aligned}$$

admits the transformations

$$x = -x', \quad y = -y', \quad z = -z',$$

but also the transformations

$$x = \xi x', \quad y = \eta y', \quad z = \zeta z',$$

where the positive constants  $\xi, \eta, \zeta$ , are governed by the equations

$$\frac{\xi^2}{\zeta} = 1, \quad \eta^2 \zeta = 1.$$

The equation  $\sin ax = b$  admits the transformation

$$x = \frac{2\pi}{a} + x'.$$

† This designation is not to be taken literally, for in such transformations a geometric similitude is not always produced. Compare remark (a) in example 2, § 9.



The most general equation of the variables  $x_1, x_2, \dots x_m$  alone will then involve an arbitrary function of a single

argument,  $\frac{x_m}{x_1^{a_1} x_2^{a_2} \dots x_{m-1}^{a_{m-1}}}$  :

$$F\left(\frac{x_m}{x_1^{a_1} x_2^{a_2} \dots x_{m-1}^{a_{m-1}}}\right) = 0,$$

which means that we must have

$$\frac{x_m}{x_1^{a_1} x_2^{a_2} \dots x_{m-1}^{a_{m-1}}} = C,$$

where the only indeterminate is the value of the constant  $C$ .

§ 4. Since problems are often treated in physics in which differential equations appear among the fundamental equations, the following comments, too, are necessary :—

1. In case one of the variables represents a differential quotient among other variables, then the system of equations must be extended by an equation which expresses this relationship, for instance :

$$x_1 = \frac{\partial^3 x_2}{\partial x_3 \partial x_4^2}.$$

This imposes a conditional equation on the transition-factors, which is easy to find. If we make in our example the transformations

$$x_1 = \xi_1 x_1'; \quad x_2 = \xi_2 x_2'; \quad x_3 = \xi_3 x_3'; \quad x_4 = \xi_4 x_4',$$

and substitute the new variables, we shall have

$$\xi_1 x_1' = \frac{\partial^3 (\xi_2 x_2')}{\partial (\xi_3 x_3') \partial (\xi_4 x_4')^2} = \frac{\xi_2}{\xi_3 \xi_4^2} \frac{\partial^3 x_2'}{\partial x_3' \partial x_4'^2}.$$

Since

$$x_1' = \frac{\partial^3 x_2'}{\partial x_3' \partial x_4'^2}$$

we must have

$$\xi_1 = \frac{\xi_2}{\xi_3 \xi_4^2}.$$

2. If in the equation sought there appear besides the variables  $x_1, x_2, \dots x_m$ , their particular values  $x_{01}, x_{02}, \dots x_{0m}$  (which is always the case when it is an integral of the given

differential equation) \*, then one must also note the transformations

$$x_{01} = \xi_{01} x_{01}' ; \quad x_{02} = \xi_{02} x_{02}' , \quad . \quad . \quad . \quad (2^{**})$$

where the transition-factors clearly are bound in the conditional equations

$$\frac{\xi_{01}}{\xi_1} = 1 ; \quad \frac{\xi_{02}}{\xi_2} = 1. \quad . \quad . \quad . \quad (3^{**})$$

§ 5. In connexion with the last comment, we may conveniently formulate the question which I previously touched only slightly †. If differential equations are included among the fundamental equations, and the equation sought is an integral of these, it will always involve particular values of the variables appearing in it, for by means of these the constants of integration may always be evaluated.

We shall therefore always have to consider more than one conditional equation ; beside the (possibly) single equation of the type

$$\frac{\xi_{r+1}}{\xi_1^{a_1} \xi_2^{a_2} \dots \xi_r^{a_r}} = 1$$

there will also be equations of the type

$$\frac{\xi_{i0}}{\xi_i} = 1.$$

Our method will therefore always render an indeterminate solution, of the type ‡

$$F \left( \frac{x_{r+1}}{x_1^{a_1} x_2^{a_2} \dots x_r^{a_r}}, \frac{x_{10}}{x_1}, \frac{x_{20}}{x_2}, \dots \right) = 0.$$

There arises the question : since most of the fundamental

\* Example : in the equation

$$s = s_0 \sin 2\pi \frac{t - t_0}{T},$$

$s_0$  is a particular value of  $s$  corresponding to  $t = t_0 + \pi/4$  ;  $t_0$  a particular value of  $t$ , corresponding to  $s = 0$  ;  $T$  a particular value of  $t$ , corresponding to the value of  $t$  required by the equation

$$\sin 2\pi \frac{t - t_0}{T} = \sin 2\pi \frac{-t_0}{T}.$$

† Conf. my article, *Math. Ann.* l. c. § 5 : "Bemerk. I." and § 14 "Behaupt. 8."

‡ Thus, for instance, the equation  $\frac{dy}{dx} = a$ , where  $a$  represents a constant of the equation, does not have the solution  $\frac{y}{ax} = \text{const.}$  which would be obtained if the particular values of  $x$  and  $y$  were forgotten



equations with which we deal in physics are differential equations, what value, in general, does the similitude-method have?

The answer is this: the derived equations in which we are interested often are not integrals of the fundamental differential equations, but relationships between only particular values of the variables and the constants of the fundamental equations†. In such cases the similitude method can readily give definite results, for then the transition-factors of the *variables* may be eliminated from the conditional equations, so that finally there is obtained a single conditional equation of only those transition-factors in which we are interested.

§ 6. In the application of the similitude-method it is important to observe the following:—

The number of independent arguments in equation (4\*) is equal to the number of conditional equations between the transition-factors under consideration. The latter may be erroneously decreased by overlooking one or another of the fundamental equations of the problem (or, as was mentioned in the preceding section, by forgetting the interdependence of the particular values of the variables). In this way there may be projected an *illusory definiteness* of solution‡. On the other hand, an *illusory indefiniteness* may occur, if one combines the transition-factors in conditional equations taken from points of view other than those called for by the similitude-method§.

and only one conditional equation  $\frac{\eta}{a\xi}$  were taken into account (where

$\eta, \xi, a$  represent the transition-factors of the transformation  $y=\eta y', x=\xi x', a=aa'$ ), but another:  $y=ax+C$ , which corresponds to the form  $F(y/ax, y_0/y, x_0/x)=0$ , for  $C$  may always be chosen so that one obtains either  $y-y_0=a(x-x_0)$  or  $y=ax$ , or  $y=ax+\frac{y_0^2}{x_0}$  etc., which

all are consistent with the form  $F=0$ . Besides, this form is still more general than the form  $y=ax+C$ , for the latter does not involve  $y=C \cdot ax$ , where  $C$  is arbitrary; this, however, is a special case of  $F=0$ . But this is permissible, for the most general solution of a given differential equation need not be the most general equation which permits the transformation corresponding to the differential equation.

† The simplest examples: (1) the period of oscillation of a gravity pendulum=function of its length, and the acceleration of gravity. (2) Kepler's equation.

‡ This is the case in the example analysed by Einstein. Footnote of the final paragraph.

§ Thus the equating, for example, of the transition-factors of all lengths, if it does not follow directly from the fundamental equations, must be considered as simply *superstitious*. Compare example 2, § 9.

In order to avoid error in the application of the similitude-method, and to obtain the greatest possible definiteness of solution, the two following rules must be observed :—

- I. *All* the fundamental equations have to be considered, of which the one desired is an analytical consequence.
- II. No conditional equations may be introduced, except those which are imposed on the transition-factors by the fundamental equations of the problem.

Both of these rules are violated in principle in the application of dimensional analysis.

### DIMENSIONAL ANALYSIS.

§ 7. Dimensional analysis teaches that the form of the equations sought is to be fixed likewise on the basis of “similitude-transformations.” Its solution, too, has the form of equation (4\*), only the conditional equations—therefore the number  $r$  of independent transition-factors and the exponents  $\alpha_{ik}$ —are not developed from the fundamental equations of the given problem, but :

1. The number of independent transition-factors is fixed once for all ; *i. e.*, they are the transition-factors of the three quantities : length, time, mass.

2. For fixing the exponents  $\alpha_{ik}$  those equations are quoted which served historically for introducing the various quantities and fixing their units, and by which the “dimension” † of each quantity is fixed.

We have as a consequence : (1) in cases where the fundamental equations of the problem have dimensional coefficients, the qualifying equations of dimensional analysis are in contradiction with those of the similitude-method ; (2) in cases where all the coefficients of the fundamental equations are dimensionless, there is of course no contradiction, but the number of conditional equations may be larger than is necessary according to the similitude-method ‡.

+ *I. e.*, a convention relative to the change of units of related quantities in dependence on the change in units of length, time, and mass. The appearance of such quantities as consequently have zero dimensions cannot be controlled according to dimensional analysis.

‡ That one may in spite of this often obtain the same conditional equations according to both methods results from this, that in general we are not excluded from obtaining the same results by elimination in two different systems of equations (conditional equations of dimensional analysis and those of the similitude-method). Cf. Ex. 1, § 9.

The number of unnecessary equations is further enlarged in dimensional analysis, in that the transition-factors of all quantities of the same sort are equated\*. Obviously the form of the equation sought does not depend on whether we designate some of its variables as physical quantities of the same kind or of the same dimensions. Hence the equating of the transition-factors of two different quantities (designated in the fundamental equations with different letters!) must be recognized as altogether a violation of rule II.†

§ 8. The last consideration may readily serve for a complete analysis of the difficulty which Mr. D. Riabouchinsky ‡ brought up in his familiar note relative to the method of Lord Rayleigh.

Lord Rayleigh availed himself of dimensional analysis, but used as independent transition-factors not three, but four: those of length, time, heat quantity, and temperature. His investigations yielded for a certain desired equation an arbitrary function of two definite arguments, which may be written:

$$h = ka\theta F\left(\frac{acv}{k}\right),$$

and which may also be written

$$\psi\left(\frac{h}{ka\theta}, \frac{acv}{k}\right) = 0.$$

Riabouchinsky thereupon showed that a greater indeterminateness would be obtained if one were to use dimensional analysis in the customary manner, with only three independent transition-factors, dealing with temperature as a "derived quantity" with the dimensions of kinetic energy. There would thus be an additional conditional equation, and consequently an additional argument in the indefinite function of the equation:

$$h = ka\theta F\left(\frac{v}{ka^2}, ca^3\right).$$

But this is an example of the violation of rule II.: the equation by which temperature is defined as the average kinetic energy of the molecules is not one of the fundamental equations of the problem; it relates temperature with

\* Cf. remark (a) in example 2 in § 9.

† In cases where in spite of this the results of the two methods are the same, it is because the ignoring of fundamental equations (lessening the number of conditional equations) and the equating of transition-factors of quantities of the same kind (increasing the number of conditional equations) compensate each other. Cf. Ex. 1. § 9.

‡ D. Riabouchinsky, "The Principle of Similitude," *Nature*, xcv. p. 591 (1915).

quantities (molecular velocity and molecular mass) which do not occur in any of the fundamental equations of the problem, and *there exists no justification for equating the transition-factors of these quantities to the transition-factors of those quantities of the same kind which actually occur in the fundamental equations.*

Besides it must be observed that if the method of Lord Rayleigh leads to good results, it is because (without his control) the actual fundamental equations of his problem involved no dimensional coefficients.

### ILLUSTRATIONS.

§ 9. The examples presented below are most trite, and yet they offer enough material for illustrating all the features of the two theories that we have discussed.

EXAMPLE 1.—To derive the relation between the time of oscillation  $T$  of a simple pendulum, its length  $l$ , and the acceleration of gravity,  $g$ .

It is assumed that such a relationship exists. The steps taken according to the method of dimensional analysis may be formulated as follows in terms of the similitude-method:—

1. Consider the equation

$$g = \frac{d^2 r}{dt^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (*)$$

where  $r$  is the distance of the pendulum from the centre of the earth. The transition-factors of the transformations

$$g = \gamma g'; \quad r = \rho r'; \quad t = \tau t'$$

are united—in order to leave the equation  $(*)$  invariant—in the conditional equation:

$$\gamma = \frac{\rho}{\tau^2}.$$

2. Because of the like nature of the physical quantities  $l$  and  $r$  the transition-factors  $\lambda$  ( $l = \lambda l'$ ) and  $\rho$  are equated:

$$\lambda = \rho.$$

3. The transition-factor  $\tau_0$  ( $T = \tau_0 T'$ ) is set equal to  $\tau$ :

$$\tau_0 = \tau,$$

since  $T$  is a particular value of  $t$ .

4. The oscillation equation

$$\frac{d^2 s}{dt^2} + \frac{g}{l} s = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (**)$$

of which the desired equation is a consequence, is ignored (!).

Thus is obtained, after elimination of  $\tau$  and  $\rho$ , the conditional equation

$$\frac{\tau_0}{\lambda^{\frac{1}{2}} \gamma^{-\frac{1}{2}}} = 1,$$

whence it follows that

$$T = c \sqrt{\frac{l}{g}}.$$

Thus steps 1 and 2 are a violation of rule II. and "step" 4 is a violation of rule I. Step 2 causes no indeterminateness because the transition-factor  $\rho$  is finally eliminated. Steps 1 and 4 compensate each other, because equations (\*) and (\*\*) fortuitously yield after the elimination of  $\rho$  and  $\tau$  the same conditional equation, which is possible because—without having previously controlled it—equation (\*\*) is homogeneous.

According to the similitude-method, the following steps would be made:—

1. Consider equation (\*\*) and derive from it the conditional equation \*

$$\frac{\sigma}{\tau^2} = \frac{\gamma}{\lambda} \sigma.$$

2. Equate the transition-factors  $\tau$  and  $\tau_0$ :

$$\frac{\tau}{\tau_0} = 1.$$

From this one will obtain after elimination of  $\tau$  the qualifying equation between just those transition-factors under consideration:

$$\frac{\tau_0}{\lambda^{\frac{1}{2}} \gamma^{-\frac{1}{2}}} = 1;$$

therefore

$$T = C \sqrt{\frac{l}{g}}.$$

This result depends only on how the quantities  $l$ ,  $g$ , and  $l$  appear in the oscillation equation (\*\*), and it would be the same even if  $g$  did not represent an acceleration, but a quantity of any kind you please †.

EXAMPLE 2.—To formulate the dependence of the time of oscillation of the pendulum on its length  $l$ , its distance  $r$  from the centre of the planet, and the attracting mass  $m$  of the planet.

\* The transition-factor  $\sigma$  thus drops out, which shows that on the basis of the similitude-method the form of the derived equations involving  $\sigma$  cannot be fixed.

† Cf. footnote to example 2.

Dimensional analysis cannot attack this problem at all, because the transition-factors of the quantities considered according to its method are quite independent of each other: in consequence of ignoring the fundamental equations of the problem it furnishes—erroneously—too few (namely, zero!) conditional equations.

According to the similitude-theory the following steps are prescribed:—

1. Consider the fundamental equations:

$$\frac{d^2s}{dt^2} + \frac{g}{l}s = 0; \quad g = k \frac{m}{r^2}, \dots \dots \dots (A)$$

whence it follows:  $\frac{1}{\tau^2} = \frac{\gamma}{\lambda}; \quad \gamma = \frac{\mu}{\rho^2}, \dots \dots \dots (B)$

where  $\mu$  and  $\rho$  are the transition-factors of the transformations  $m = \mu m'$  and  $r = \rho r'$ , respectively.

2. Put

$$\tau_0 = \tau. \dots \dots \dots (B')$$

In the equation sought the quantities  $t$  and  $g$  are not to appear; we must therefore see whether they may be eliminated from (B) and (B'). They may; and thus we obtain in consequence a single conditional equation:

$$\frac{\tau_0}{\lambda^{\frac{1}{2}} \rho \mu^{-\frac{1}{2}}} = 1,$$

whence it follows that

$$T = Cr \sqrt{\frac{l}{m}}.$$

*Remarks.*—(a) Equating the transition-factors  $\rho$  and  $\lambda$ —in violation of rule II.—would create an additional conditional equation of the transition-factors under consideration,  $\frac{\rho}{\lambda} = 1$ , and would cause an illusory indeterminateness, for then we should have the equation

$$F\left(\frac{T}{r^{\frac{1}{2}} m^{-\frac{1}{2}}}, \frac{r}{l}\right) = 0,$$

which would permit the form

$$T = Cr \sqrt{\frac{l}{m}}$$

as well as

$$T = Cl \sqrt{\frac{r}{m}} \quad \text{and} \quad T = C_1 \sqrt{\frac{l^3}{m}} + C_2 \sqrt{\frac{r^3}{m}},$$

and as many others as you please.

(b) With the aid of the similitude-method we can investigate *selectively* the part played in the equation sought by

just those quantities which interest us, without caring about the others; *i. e.*, we may apply those similitude-transformations in which all the other quantities are unchanged. Thus, for example, we may obtain the following relationship of  $T$ ,  $l$ , and  $m$  only (by putting  $\rho = 1$ ):

$$\frac{\tau_0}{\lambda^{\frac{1}{2}} \mu^{-\frac{1}{2}}} = 1;$$

therefore 
$$T = C \sqrt{\frac{l}{m}},$$

in which  $c$  remains constant only while  $\frac{k}{r^2}$  remains constant.

If we want to know how the gravitational constant  $k$  affects the time of oscillation, we have to introduce the transformation equation  $k = \kappa k'$  among the others (which is independent of whether or not  $k$  is a universal constant), and we then obtain:

$$\frac{\tau_0}{\rho \lambda^{\frac{1}{2}} \mu^{-\frac{1}{2}} \kappa^{-\frac{1}{2}}} = 1;$$

therefore 
$$T = Cr \sqrt{\frac{l}{km}}.$$

#### CONCLUSION.

§ 10. According to this comparison of dimensional analysis with the similitude-method, we see that only the latter yields results essentially dependable, even though often not very definite. However, if the fundamental equations of the problem are unknown, of the two methods there remains only dimensional analysis. It must never be forgotten that in such cases one advances only gropingly, and without experimental or theoretical proof from another quarter one can never be completely certain of the results. Dimensional analysis combined with proof of this kind may be viewed as a systematic method for determining whether in the given problem new and unknown fundamental equations take part which are non-homogeneous relative to the quantities considered; *i. e.* which involve dimensional coefficients or new variables †.

Leiden, Aug. 30, 1925.

\* We see that here the quantity  $m$  is in exactly the same position as the quantity  $g$  in example 1, although it has a different dimension! And that is because it is in the same position in the fundamental equation of this example, as  $g$  in that of example 1.

† A pretty example of such an application of dimensional analysis is found in the paper of A. Einstein; cf. "Zum gegenwärtigen Stand des Strahlungsproblems," *Phys. Zschr. x.* § 6, p. 189 (1909).

**XVIII. The Roots of Hypergeometric Functions with a numerator and four denominators.** By H. E. H. WRINCH, *M.I.Mech.E., and D. M. WRINCH, M.A., D.Sc.\**

**D**URING the last few years, the Generalized Hypergeometric Function has become of increasing importance in applied mathematics. This paper contains certain tables of the roots of certain generalized hypergeometric functions which have important applications in the theory of the vibrations of bars of various cross-sections. Attention was called to the fundamental significance in problems of morphology of the periods of vibration of bars of varying density with cross-sections of various types by Dendy and Nicholson † in 1917.

In the present paper we give roots of the equation

$$F(\alpha; \alpha_1, \alpha_2, \alpha_3, \alpha_4; -4(x/4)^4) = 0$$

—for a large range of values of the parameters  $(\alpha, \alpha_1, \alpha_2, \alpha_3, \alpha_4)$

—where  $F$  is the generalized hypergeometric function with one numerator and four denominators,

$$F(\alpha; \alpha_1, \alpha_2, \alpha_3, \alpha_4; -4(x/4)^4)$$

$$\equiv 1 - \frac{4(1+\alpha)(x/4)^4}{1!(1+\alpha_1)(1+\alpha_2)(1+\alpha_3)(1+\alpha_4)}$$

$$+ \frac{4^2(1+\alpha)(2+\alpha)(x/4)^8}{2!(1+\alpha_1)(2+\alpha_1)(1+\alpha_2)(2+\alpha_2)(1+\alpha_3)(2+\alpha_3)(1+\alpha_4)(2+\alpha_4)}.$$

These roots are required for an investigation ‡ which develops the general idea put forward by Dendy and Nicholson in the paper already cited and by Dendy in a number of other publications §.

The full discussion of the roots of the equation would require the consideration of the various values taken by the five separate parameters. Such a discussion is not required for the applications under contemplation, though it could be carried out on similar lines.

The special values of the parameters to be included in the

\* Communicated by the Authors.

† Proc. Roy. Soc. A, vol. xciii.; Proc. Roy. Soc. B, vol. lxxxix.

‡ Wrinch, Phil. Mag. vol. xlv. (1923).

§ See, for example, Dendy's Presidential Address to the Quekett Microscopical Club, Journ. Q. M. C. series 2, vol. xiii. (1917). Cp. also Nicholson, "The Lateral Vibrations of Sharply-pointed Bars," Proc. Roy. Soc. A, vol. cxvii. (1921).



present discussion are specified as follows : —

Let

$$\alpha_1, \alpha_2, \alpha_3, \alpha_4 = \frac{7s}{4} - 2, \frac{3s}{2} - 2, \frac{5s}{4} - 2, 3s - 4;$$

$$\alpha = 3s - \frac{9}{2}^*.$$

TABLE I.— $s = 1$ .

No. of Root.	$x$ .
1 .....	1.571
2 .....	4.712
3 .....	7.854
4 .....	10.996
5 .....	14.137
6 .....	17.279
7 .....	20.420
8 .....	23.562
9 .....	26.704

TABLE II.— $s = 20/19$ .

No. of Root.	$x$ .
1 .....	1.891
2 .....	4.987
3 .....	8.118
4 .....	11.255
5 .....	14.394
6 .....	17.534
7 .....	20.675
8 .....	23.816
9 .....	26.956

TABLE III.— $s = 20/18$ .

No. of Root.	$x$ .
1 .....	2.213
2 .....	5.283
3 .....	8.407
4 .....	11.541
5 .....	14.678
6 .....	17.816
7 .....	20.956
8 .....	24.096
9 .....	27.236

TABLE IV.— $s = 20/17$ .

No. of Root.	$x$ .
1 .....	2.544
2 .....	5.606
3 .....	8.725
4 .....	11.856
5 .....	14.992
6 .....	18.129
7 .....	21.268
8 .....	24.408
9 .....	27.548

TABLE V.— $s = 20/16$ .

No. of Root.	$x$ .
1 .....	2.894
2 .....	5.958
3 .....	9.076
4 .....	12.206
5 .....	15.341
6 .....	18.478
7 .....	21.617
8 .....	24.756
9 .....	27.896

TABLE VI.— $s = 20/15$ .

No. of Root.	$x$ .
1 .....	3.270
2 .....	6.347
3 .....	9.468
4 .....	12.598
5 .....	15.734
6 .....	18.871
7 .....	22.009
8 .....	25.149
9 .....	28.289

\* The quantity  $s$  has special significance in the application in question in connexion with the shape of the vibrating rod. See Wrinch, *loc. cit.* p. 275.

TABLE VII.— $s = 20/14$ .

No. of Root.	$x$ .
1 .....	3.682
2 .....	6.781
3 .....	9.907
4 .....	13.040
5 .....	16.177
6 .....	19.315
7 .....	22.455
8 .....	25.594
9 .....	28.735

TABLE VIII.— $s = 20/13$ .

No. of Root.	$x$ .
1 .....	4.142
2 .....	7.269
3 .....	10.405
4 .....	13.543
5 .....	16.683
6 .....	19.823
7 .....	22.964
8 .....	26.105
9 .....	29.246

TABLE IX.— $s = 20/12$ .

No. of Root.	$x$ .
1 .....	4.665
2 .....	7.826
3 .....	10.975
4 .....	14.121
5 .....	17.266
6 .....	20.409
7 .....	23.553
8 .....	26.695
9 .....	29.838

TABLE X.— $s = 20/11$ .

No. of Root.	$x$ .
1 .....	5.270
2 .....	8.469
3 .....	11.637
4 .....	14.794
5 .....	17.946
6 .....	21.094
7 .....	24.241
8 .....	27.387
9 .....	30.531

TABLE XI.— $s = 2$ .

No. of Root.	$x$ .
1 .....	5.985
2 .....	9.226
3 .....	12.417
4 .....	15.589
5 .....	18.750
6 .....	21.906
7 .....	25.058
8 .....	28.208
9 .....	31.356

Then, we give a number of roots of the equation when  $s$  has the values

$s = 20/20, 20/19, 20/18, 20/17, 20/16, 20/15,$

$20/14, 20/13, 20/12, 20/11, 20/10$

intermediate between  $s = 1$  and  $s = 2$ . The roots are found

obtained by means of the asymptotic expansion for the hypergeometric function obtained by one of the present writers \* in 1923.

*Note.*—We are indebted to the Government Grant Committee of the Royal Society for a grant in aid of the computations contained in this paper.

**XIX. The Field of a Thick Spherical Shell on Einstein's Theory of Relativity.** By J. T. COMBRIDGE, M.A., M.Sc. (Imperial College of Science) †.

THE only problem to which Einstein's gravitational equations for the field in attracting matter appear to have been applied is that of a sphere containing a perfect fluid. Opinion is divided as to what restrictions on the components of the "material-energy-tensor" are necessary for the definition of a perfect fluid, but these restrictions are always imposed and the components (pressures and density) specified before a solution of the gravitational equations is attempted ‡. It is, however, possible to extract a great deal of useful information with fewer restrictions. We shall here confine ourselves to a heterogeneous shell such that the layers of equal density are concentric spheres.

From considerations of spherical symmetry we assume that with spherical polar coordinates with their origin at the centre of the shell the quadratic form may be taken as

$$ds^2 = -e^\lambda dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta d\phi^2 + e^\nu dx_4^2, \quad (1)$$

where  $\lambda$  and  $\nu$  are functions of  $r$  only, and  $x_4 = ct$ ,  $c$  being the velocity of light *in vacuo* in the absence of gravitation. Similarly we assume for the components  $T^{\alpha\beta}$  of the material-energy-tensor

$$\left. \begin{array}{l} T^{\alpha\beta} \text{ functions of } r \text{ only, and} \\ T^{\alpha\beta} = 0 \text{ unless } \alpha = \beta. \end{array} \right\} \quad \dots (2)$$

$T^{11}$ ,  $T^{22}$ ,  $T^{33}$  are pressures, and  $T^{44}$  is the density referred to the coordinates in use. All are zero except at points occupied by matter. The mixed components  $T_a^\beta$  are given by

$$T_a^\beta = g_{\alpha\gamma} T^{\beta\gamma}$$

\* Phil. Mag. vol. xlv. (1923).

† Communicated by Prof. G. B. Jeffery, M.A., D.Sc.

‡ Cf. de Donder, 'La Gravifique einsteinienne,' p. 54; Eddington, 'Mathematical Theory of Relativity' (2nd ed.).



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new condition. Instead of (7), (8), and (9) above, we use (7) + (8) + (9) and (7) + (9), together with equation (4). The first of these gives

$$-\frac{2}{r}\dot{\lambda} + \frac{2}{r^2}(1 - e^\lambda) = -4\kappa e^\lambda T_4^4,$$

whence

$$e^\lambda = \left\{ 1 - \frac{2}{r}m(r) \right\}^{-1}, \quad . \quad . \quad . \quad (10)$$

where

$$m(r) \equiv \kappa \int_0^r T_4^4 r'^2 dr'. \quad . \quad . \quad . \quad (11)$$

The second gives

$$-\frac{1}{r}(\dot{\lambda} + \dot{\nu}) = 2\kappa(T_1^1 - T_4^4)e^\lambda,$$

whence

$$\lambda + \nu = 2\kappa \int_0^r r' e^\lambda (T_4^4 - T_1^1) dr,$$

and so

$$e^\nu = \left\{ 1 - \frac{2}{r}m(r) \right\} e^{\int_0^r F(r') dr'} \quad . \quad . \quad . \quad (12)$$

with

$$F(r) \equiv 2\kappa r \left\{ 1 - \frac{2}{r}m(r) \right\}^{-1} (T_4^4 - T_1^1) \quad . \quad . \quad . \quad (13)$$

If it is desired to specify further the nature of the material composing the shell, the corresponding relation between  $T_1^1$ ,  $T_2^2$  and  $T_4^4$  may be laid down. From this  $T_2^2$  may be eliminated since it is given explicitly by (4), leaving a relation between  $T_1^1$  and  $T_4^4$ . If in addition the density-component  $T_4^4$  be given as a function of  $r$ , the problem is completely determinate. What is, however, of greater interest is the conclusion to be derived from the above results regarding the field in the interior of the shell.

Let  $a$  and  $b$  be the radii of the bounding surfaces of the shell ( $b > a$ ). Then for  $a \geq r \geq 0$ ,  $T_a^a = 0$  and so  $m(r)$  and  $F(r)$  are both zero. Hence in the cavity of the shell  $e^\lambda$  and  $e^\nu$  are both constants and space-time is Euclidean. This is a particular case of the analogy of the theorem in classical potential-theory that the potential is constant in the cavity of such a shell.

For  $r \geq b$ ,

$$m(r) = \kappa \int_a^b T_4^4 r'^2 dr'; \quad \int_0^r F(r') dr' = \int_a^b F(r') dr'.$$

since  $T_1^1$  and  $T_4^4$  are zero except for values of  $r$  between  $a$  and  $b$ . But these being definite integrals are both constants. Denote the former by  $M$  and the latter by  $k$ . Then

$$e^A = \left(1 - \frac{2M}{r}\right)^{-1} \quad \text{and} \quad e^v = e^k \left(1 - \frac{2M}{r}\right).$$

Comparing these values with those of the usual solution for the field of the sun, we see that the constant of integration  $M$  in that solution is really  $\kappa \int_0^R T_4^4 r^2 dr$ , where  $R$  is the sun's radius\*. The establishment in this manner of the identity of the constant of integration with the inertial mass is believed to be new. It does not require, as Schwarzschild's work does, the assumption that  $T_4^4$  is constant throughout the sphere. Identity with the gravitational mass follows as usual from the equations of motion.

For  $b \geq r \geq a$ , the expressions for  $m(r)$  and  $F(r)$  exist only between the limits  $a$  and  $b$ , and so the "potentials" over any spherical surface of radius  $r$ , concentric with the origin and lying in the material, are those due to a spherical shell whose inner and outer radii are  $a$  and  $r$  respectively, the matter outside the surface again contributing nothing to the field. The analogy with a classical theorem is once more obvious.

XX. *On the Absolute Value of Entropy.* By MEGHNAD SAHA, D.Sc., Professor of Physics, Allahabad University, and RAMANIKANTA SUR, M.Sc., Government Intermediate College, Allahabad †.

ACCORDING to Boltzmann, the entropy of a thermodynamical system is represented by the equation

$$S = k \log_e W. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$S$  = entropy,  $k$  = Boltzmann's gas-constant,  $W$  = probability of the state.

There are different ways of calculating the probability  $W$  for different thermodynamical systems. In previous years,  $W$  was used in a relative sense, in terms of some standard state. By  $W$  was meant the mathematical probability,

\* If  $e^v$  is to be unity when  $r$  is infinite,  $k$  must be zero.

† Communicated by the Authors.

hence it was always a fraction. Moreover, it remained indeterminate to the extent of an additive constant.

To Planck we owe the conception of the "Thermodynamical probability." This is proportional to the mathematical probability, but not quite equal to it. The mathematical probability is a fraction, while the thermodynamical probability is a whole number. Planck has developed methods for calculating the thermodynamical probability of different systems—*e.g.*, a perfect gas and black body radiation. As is well known, this idea led, in the hands of its author, to the development of the Quantum theory, which is now responsible for progress along all lines in physical science.

There are, however, a few points which are not yet clear. Some of these refer to the fundamental assumptions of the theory, others refer to the mode of application of the fundamental ideas. The exact nature of these obscure points can only be made clear by reference to the actual working, which we now proceed to do.

### § 1. *Theory of Perfect Gases\*.*

Let us take a large number  $N$  of molecules enclosed within a volume  $V$  in the gas-kinetic sense. To calculate the probability of the system, the volume is divided into a number of cells denoted by 1, 2, 3, ...,  $n$ , containing  $N_1, N_2, N_3, \dots, N_n$  molecules respectively. The thermodynamical probability is defined as the total number of complexions (*i.e.*, the total number of ways in which this distribution can be effected). It is easy to see that

$$W_n = \frac{N!}{N_1! N_2! \dots N_n!} \cdot \dots \cdot \quad (2)$$

The mathematical probability

$$W_{mn} = \frac{W_n}{\sum W_n} = W_n \cdot n^{-N}. \quad \dots \cdot \quad (2.1)$$

The summation  $\sum W_n$  is taken over all positive values of  $N_1, N_2$ , etc. consistent with the condition

$$N_1 + N_2 + \dots N_n = N.$$

$$\text{Let} \quad \frac{N_1}{N} = w_1, \quad \frac{N_2}{N} = w_2, \dots$$

\* The subject matter of this section is merely an abstract of § 113-§ 134 of Planck's 'Wärmestrahlung,' 5th edition.

Then with the help of Stirling's formula, it can be easily shown that

$$\log W_n = -N \sum_{r=1}^{r=n} w_r \log w_r. \quad (3)$$

The actual or equilibrium value of  $\log W_n$  is obtained by making it maximum subject to the prescribed conditions. Let  $\epsilon_r$  = average energy per molecule in the cell  $r$ . Then the total energy

$$\begin{aligned} E &= N_1 \epsilon_1 + N_2 \epsilon_2 + \dots + N_n \epsilon_n \\ &= N \sum w_r \epsilon_r = \text{const.} \end{aligned} \quad (4)$$

and  $\sum w_r = 1. \quad (5)$

From equations (3), (4), (5), we can deduce that in case of equilibrium

$$w_r = \alpha e^{-\beta \epsilon_r}. \quad (6)$$

From the relation  $\frac{\partial S}{\partial E} = \frac{1}{T}$  it can be shown that

$$\beta = \frac{1}{kT}. \quad (7)$$

From equations (5) and (6)

$$\alpha = \frac{1}{\sum e^{-\epsilon_r/kT}}, \quad (8)$$

and it can easily be shown that the free energy

$$F = kNT \log \alpha; \quad (9)$$

$\alpha$ , however, remains indeterminate, and it cannot be calculated without the introduction of some further hypothesis.

By an application of Liouville's law, Planck shows that for a system obeying the canonical laws of Hamilton the motion is completely defined if the positional ( $q$ ) and the momenta ( $p$ ) coordinates corresponding to each individual degree of freedom of each particle are given. In this case he shows that the phase integral

$$H = \dots \iiint \dots dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f \quad (10)$$

(the integral being taken for all the degrees of freedom for a particle), remains unchanged by subsequent events.  $H$  is known as the extension of the elementary region of the phase space. According to classical theory,  $H$  may have any infinitely small value up to zero, but according to the



quantum theory  $H$  has always got a finite, though small, invariant value.

The summation  $\sum e^{-\frac{\epsilon_n}{kT}}$  can now be effected.

$$\sum e^{-\frac{\epsilon_n}{kT}} = \frac{\sum e^{-\frac{\epsilon_n}{kT}} dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f}{H} \quad (11)$$

For monatomic gases,  $H$  must refer to the representative particle in the cell  $r$ , having the coordinates  $x_r, y_r, z_r$ , and velocity components  $u_r, v_r, w_r$ .

$$\text{Taking} \quad \epsilon_r = \frac{1}{2}m(u_r^2 + v_r^2 + w_r^2) + \epsilon_0, \quad (12)$$

where  $\epsilon_0$  denotes the unalterable internal energy of an atom at rest, and

$$dp_1 dp_2 dp_3 = m^3 du_r dv_r dw_r.$$

We obtain

$$\sum e^{-\frac{\epsilon_r}{kT}} = \frac{V}{H} e^{-\frac{\epsilon_0}{kT}} (2\pi mkT)^{3/2}. \quad (13)$$

With this value of  $\sum e^{-\frac{\epsilon_r}{kT}}$ , neglecting  $\epsilon_0$ ,

$$S = kN \left\{ \frac{V}{H} (2\pi mkT)^{3/2} \right\} + \frac{3}{2}kN. \quad (14)$$

According to the classical gas laws,

$$S = kN \log \{ VT^{3/2} \} + i, \quad (14.1)$$

where  $i$  is independent of  $T$  and  $V$ , but depends upon  $N$ . As far as the calculation of gas laws and specific heat is concerned, the exact value of  $i$  is immaterial; but if we wish to study the chemical behaviour of the gas, the vapour pressure, etc., the knowledge of  $i$  is essential, as was first pointed out by Nernst in connexion with his Heat Theorem.

Now to show how  $i$  depends upon  $N$  we take  $p$  identical vessels, each of volume  $V$ , containing the same quantity of the same gas side by side. Then suppose the sides be made to collapse suddenly and the  $p$  volumes are made to mix with each other. No change has been made in the system. The entropy can be calculated by adding the entropies of the  $p$  vessels, each of volume  $V$ . Thus for the entropy of the whole gas occupying the volume  $pV$  we have

$$S = kNp \log (VT^{3/2}) + pi(N), \quad (14.2)$$

and this must equal

$$k\overline{N}p \log (\overline{p}\overline{V} \cdot T^{3/2}) + i(pN),$$

which is the entropy of a gaseous mass of  $p\overline{N}$  particles occupying the volume  $\overline{p}\overline{V}$ .

Hence  $pi(N) = kNp \log p + i(pN)$ .

The above relation is satisfied if

$$i(N) = -kN \log N.$$

Thus we can deduce from the classical theory that

$$S = kN \log \left[ \frac{V}{N} T^{3/2} A \right], \dots \dots (14.3)$$

where  $A$  is independent of  $N$ ,  $T$ , and  $V$ .

From Planck's theory, we have

$$S = kN \log \left[ \frac{V}{H} (2\pi mkT_e)^{3/2} \right] \dots \dots (14)$$

Comparing the two expressions, we find that  $H$  must vary as  $N$ . Planck puts  $H = N/h^3$ . But this is, however, not quite clear from the expression for  $H$ , for

$$H = \left\{ \int \int d q_1 d p_1 d q_2 d p_2 d q_3 d p_3 \right\} / h^3 \dots \dots (15)$$

if we put, according to the canons of the quantum theory,

$$\int \int d q \cdot d p = h \text{ (Planck's constant).}$$

Sackur and Tetrode\*, who were the first to calculate the value of  $i$ , proceeded in a different way. According to Sackur the thermodynamic probability is not equal to our  $W_n$ , but it is equal to

$$\frac{W_n}{N!} \text{ or } \frac{1}{N_1! N_2! \dots N_n!}.$$

The value of  $H$ , according to Sackur, is

$$\int \int d q_1 d p_1 d q_2 d p_2 d q_3 d p_3 = h^3.$$

Tetrode's procedure was identical.

Attention to this point has recently been called by Ehrenfest and Trkal†, who have introduced a new method of dealing with the thermodynamical problems, *e. g.* dissociation equilibrium and vapour pressure, in which all these difficulties are avoided. We shall return to this method shortly. Planck has justified his assumption, *viz.*  $H = N/h^3$ , by taking into account the permutability of the molecules, but the reasoning is rather difficult to follow.

\* Sackur, *Ann. d. Physik*, xl. Tetrode, *loc. cit.* xxxix.

† Ehrenfest and Trkal, *Proc. Amst. Akad.* xxiii. (1920).

§ 2. *Ehrenfest's Method.*

Ehrenfest has introduced a very general method for dealing with the thermodynamical behaviour of different and complex systems, like mixtures of gases reacting with each other. We shall confine our attention to the case of perfect gases.

Ehrenfest replaces the entropy function  $S$  by another function  $\{\gamma\}$  which is allied but not equal to  $W$ .  $\{\gamma\}$  is supposed to represent the total phase space described by the system and is defined in the following way:—Let the system consist of  $N$  particles. Then each particle describes a sub-phase space  $\{\mu\}$ , where

$$\{\mu\} = \dots \int \dots dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f. \quad (16)$$

The total  $\{\gamma\}$ -space described by the system is then given by

$$\{\gamma\} = P \prod_N \{\mu\}, \quad . \quad . \quad . \quad (17)$$

the product extending over all the particles.  $P$  represents the permutability of the particles.

Now, in our case, i. e., for monatomic gases,

$$\{\gamma\} = \dots \int \int \int \dots dx_r dy_r dz_r d(mu_r) d(mv_r) d(mw_r), \quad (17.1)$$

$$mu_r = p_{1r}, \quad mv_r = p_{2r}, \quad mw_r = p_{3r}.$$

$$\text{Now} \quad \Sigma p_{1r}^2 + p_{2r}^2 + p_{3r}^2 = 2mE, \quad . \quad . \quad . \quad (17.2)$$

where  $E$ =total kinetic energy and  $m$  is the mass of a particle.

$$\text{Hence} \quad \{\gamma\} = \frac{V^N (2\pi m E)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)}. \quad . \quad . \quad . \quad (18)$$

$$\text{Putting now} \quad E = \frac{3N}{2} kT,$$

$$\log \{\gamma\} = N \log \{V(2\pi m k T)^{3.2}\}. \quad . \quad . \quad (19)$$

According to Sackur-Tetrode:—

$$S = kN \log \left\{ e^{5/2} \frac{V}{N h^3} (2\pi m k T)^{3.2} \right\}$$

$$= k \log W.$$

Comparing the two expressions,

$$W = \frac{\{\gamma\}}{h^{3N} N!} \cdot . \quad . \quad . \quad (20)$$

## § 3.

Ehrenfest and Trkal have not traced any connexion between  $\{\gamma\}$  and  $W$ . But from equations (18), (19), and (20), it is possible not only to connect  $W$  and  $\{\gamma\}$  for any general system, but also to lay down a general theorem for the calculation of the probability of any system. This we now proceed to do.

According to Planck, the probability  $W$  is a whole number. But whenever in physics we wish to determine the absolute value of any quantity, we must as well lay down a "unit" for it. Now let us see what is meant by "Unit Probability."

The idea of "Unit Probability" is intimately connected with the zero of entropy; for  $S = k \log W$ , and when  $W = 1$ ,  $S = 0$ . According to the second law of thermodynamics, this takes place when a condensed system is reduced to absolute zero; for a reversible engine acting between this system and another system at a finite temperature  $T$  will be able to convert all the heat energy abstracted into mechanical work.

We can suppose this to take place in another way. Suppose we have a gas at a finite temperature. The particles are moving in a chaotic way and at a distance from each other. Suppose all of them suddenly begin to move with identical velocity in the same direction, with the proviso, however, that the total kinetic energy remains the same. Then if this system, on coming into contact with another body and suffering inelastic collision, transfers the whole of its energy to that body, we can say that the heat motion has been completely converted into mechanical work. Thus the idea of absolute zero, and zero of entropy, presupposes a system of particles absolutely devoid of all motion. But this is not sufficient. If the particles which are devoid of all motion remain at a distance from each other, then, owing to mutual attraction and there being no motion, they will begin to move towards each other, and kinetic energy will again be developed and can again be converted into mechanical work. For an attracting system, motion, and with it the energy available from the system, will entirely stop when the particles are packed together in the closest manner possible.

We assume that such a system possesses unit probability. Let the value of  $\gamma$ -space for such a system be denoted by  $\{\gamma\}$ .

We may remark here that these considerations apply only if we regard the atoms as the final constituents of matter.

This, however, is not the case, and therefore, even when the state pictured above has been reached, the electrons of one atom will react mechanically on the other atoms and electrons; and motion will never be entirely absent. Thus we cannot conceive of an absolute zero of temperature unless we picture to ourselves a state in which the protons and electrons have combined in some unknown way and annihilated all matter. We can therefore talk of absolute zero in a world where there is no matter. But according to the generalized theory of relativity, there can be neither space, time, nor any physical quantity in a world which is entirely devoid of matter. Hence we come to a conclusion which has been previously reached by Nernst, viz., in the phenomenal world it is impossible to reach the absolute zero of temperature.

We shall now proceed to calculate the thermodynamical probability of a system in the terms of  $\{\gamma\}_0$  as unity. The probability of the state of a system is proportional to the phase space  $\{\gamma\}$  described by the system. Therefore the thermodynamical probability at a finite temperature

$$W = \frac{\{\gamma\}}{\{\gamma\}_0} \quad \dots \quad (21)$$

We have now to find out the value of  $\{\gamma\}_0$ .

Let us suppose that in the system there are  $N$  particles, each particle having  $f$  degrees of freedom. We shall follow Ehrenfest's considerations in calculating  $\{\gamma\}_0$ . According to the definition, for a single particle

$$\{\mu\} = \dots \iint \dots dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f \quad \dots \quad (16)$$

Let us suppose that each particle is a Planck-resonator and confine our attention to one degree of freedom only. According to the quantum theory its phase-point  $(q, p)$  must lie at  $p=0$ ,  $q=0$ , or on one of the ellipses  $h, 2h, \dots$ , the area between two consecutive ellipses being given by

$$\iint dq dp = h^*.$$

Ehrenfest attaches a "weight"  $h$  to each one of these ellipses, and in particular also to the point  $(p=0, q=0)$ . Now, in our case, i. e., for a system at absolute zero, none of the degrees of freedom of any particle is excited: or the phase of every particle for each degree of freedom is at  $(p=0, q=0)$ .

\* Vide Ehrenfest and Trkal, Proc. Amst. Soc. xxiii. p. 179 (1920).

Hence, for a single particle,

$$\{\mu\} = \dots \iint \dots dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f \\ = h^f.$$

For the whole system

$$\prod_N \{\mu\} = h^{fN}. \quad (22)$$

Again the  $N$  particles can be arranged amongst themselves in  $N!$  ways. Combining this with (22), we obtain

$$\{\gamma\}_0 = h^{fN} N!. \quad (23)$$

To sum up, the thermodynamic probability in Planck's sense is given by

$$W = \frac{\{\gamma\}}{h^{fN} \cdot \underline{N}}. \quad (20.1)$$

This will cover all cases.

On the basis of this law we shall now calculate the entropy of a system consisting of diatomic molecules.

#### § 4. Entropy of a Gas consisting of Diatomic Molecules.

In this case we shall ignore the rotation of molecules about the axis of symmetry and also all internal motions of atoms in the molecule. Therefore, each molecule has only five degrees of freedom, three of these being translational and two rotational.

Thus

$$\{\gamma\}_0 = h^{5N} \underline{N} \\ = h^{5N} N, \quad (24)$$

where  $N$  denotes the total number of molecules considered.

Now, for a single molecule,

$$\{\mu\} = \int \dots dx dy dz d\theta d\psi dp_1 dp_2 dp_3 dp_4 dp_5 \\ = V \cdot 4\pi \cdot \int \dots dp_1 \dots dp_5. \quad (25)$$

Therefore  $\gamma$ -space for the total system is given by

$$\{\gamma\} = \prod_N \{\mu\} \\ = V^N \cdot (4\pi)^N \cdot \int \dots dp_{1r} dp_{2r} \dots dp_{5r} \dots, \quad (26)$$

the integrals being taken for all molecules,  $dp_{1r}$ ,  $dp_{2r}$ , etc. denote the momenta of the different molecules.

The total kinetic energy of the molecules being given, the integration is to be taken over all possible values of the

momenta which are consistent with it. If  $E$  be the kinetic energy given, we have

$$\sum \frac{p_{1r}^2}{2m} + \frac{p_{2r}^2}{2m} + \frac{p_{3r}^2}{2m} + \frac{p_{4r}^2}{2a} + \frac{p_{5r}^2}{2b} = E, \quad \dots \quad (27)$$

where  $m$  is the molecular mass and  $a$  and  $b$  represent the moments of inertia. The molecules being all similar, these quantities ( $m$ ,  $a$ , and  $b$ ) have the same values for all the molecules. The total number of terms in the left-hand side of equation (27) is  $5N$ .

Hence

$$\begin{aligned} \{\gamma\} &= V^N \cdot (4\pi)^N \cdot \int \dots dp_{1r} dp_{2r} \dots dp_{5r} \dots \\ &= V^N \cdot (4\pi)^N \cdot \sqrt{\pi}^{5N} \cdot \frac{\sqrt{E^{5N-1}}}{\left(\frac{5N}{2}\right)} \cdot \{(2m)^{3/2} \cdot (2a)^{1/2} \cdot (2b)^{1/2}\}^N, \end{aligned} \quad \dots \quad (28)$$

since  $N$  is very large, we may put  $5N$  for  $5N-1$ .

$$\begin{aligned} \{\gamma\} &= V^N \cdot (4\pi)^N \cdot \frac{\sqrt{2\pi E^{5N}}}{\left(\frac{5N}{2}\right)} \cdot (m^{3/2} \cdot a^{1/2} \cdot b^{1/2})^N \\ &= \frac{V^N \cdot (4\pi)^N \cdot \sqrt{2\pi E^{5N}} \cdot (m^{3/2} \cdot a^{1/2} \cdot b^{1/2})^N}{\left(\frac{5N}{2}\right)!} \quad (28.1) \end{aligned}$$

Hence

$$\begin{aligned} W &= \frac{\{\gamma\}}{\{\gamma\}_0} = \frac{\{\gamma\}}{h^{5N} \cdot N!} \quad \dots \quad (29) \\ &= \frac{V^N \cdot (4\pi)^N \cdot \sqrt{2\pi E^{5N}} \cdot (m^{3/2} \cdot a^{1/2} \cdot b^{1/2})^N}{h^{5N} \cdot N! \left(\frac{5N}{2}\right)!} \quad (29.1) \end{aligned}$$

Using Stirling's formula and putting  $E = \frac{5}{2} NkT$ , we obtain

$$\begin{aligned} W &= \left\{ \frac{e^{7/2} \cdot 4\pi V \cdot (2\pi kT)^{5/2} \cdot m^{3/2} \cdot a^{1/2} \cdot b^{1/2}}{N \cdot h^5} \right\}^N \quad (29.2) \\ S &= k \log W \\ &= Nk \log \left\{ \frac{e^{7/2} \cdot 4\pi V \cdot m^{3/2} \cdot a^{1/2} \cdot b^{1/2} \cdot (2\pi kT)^{5/2}}{N \cdot h^5} \right\} \quad (30) \end{aligned}$$

It may be emphasized here that the theorems  $E = \frac{3}{2} NkT$  for monatomic gases and  $E = \frac{5}{2} NkT$  for diatomic gases have not been assumed here, but followed directly from the theory. The calculations have not been reproduced here.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

1.

Hydrogen.

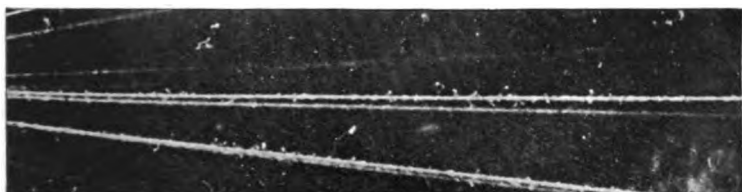
$\times 3.8$



2.

Helium.

$\times 2.3$



3.

Argon.

$\times 3.3$



4.

Hydrogen.

$\times 4.4$







5.

Hydrogen.

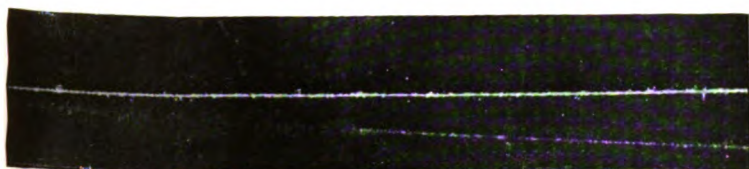
$\times 3.6$



6.

Hydrogen.

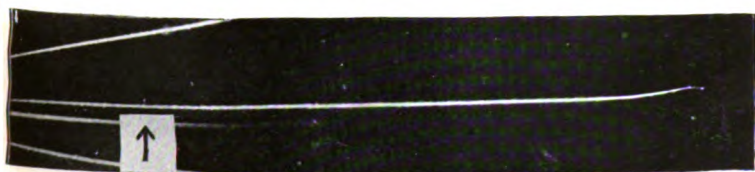
$\times 3.6$



7.

Hydrogen.

$\times 2.0$



8.

Helium.

22

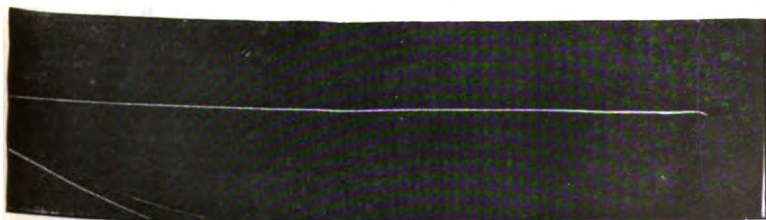




FIG. 2.



FIG. 3.





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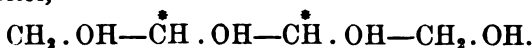
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[SEVENTH SERIES.]

FEBRUARY 1926.

XXI. *An X-Ray Examination of i-Erythritol.*  
By W. G. BURGERS (*Rockefeller Foundation Fellow*) \*.

THE present paper deals with the X-ray examination of an organic compound of relatively simple constitution, *i*-erythritol,



The investigation was undertaken mainly to determine the symmetry of the crystal-molecule. Erythritol is one of the simplest compounds with two so-called "asymmetric" carbon-atoms (indicated in the formula by asterisks), and moreover two which are linked with exactly similar groups of atoms. A difference in the spatial arrangement of these groups with regard to the "asymmetric" carbon-atoms is possible. This gives rise to the existence of a right-handed and a left-handed form, a racemic form, and an internally-compensated or meso form. The compound is wholly comparable with tartaric acid.

In figs. 1 and 2 the different forms are represented in the usual schematic way. The "asymmetric" carbon-atoms (which are not represented in the figures) occupy corresponding positions within the tetrahedra. According to the conventions of stereochemistry, the configurations in these figures are drawn in the most symmetrical way.

A and B are two possibilities of the same active form (B has been obtained from A by rotating the upper tetrahedron through  $180^\circ$  about the bond between the two

\* Communicated by Sir William Bragg, K.B.E., F.R.S.



asymmetric carbon-atoms). They have a two-fold axis as the only symmetry-element, and are therefore different from

Fig. 1.

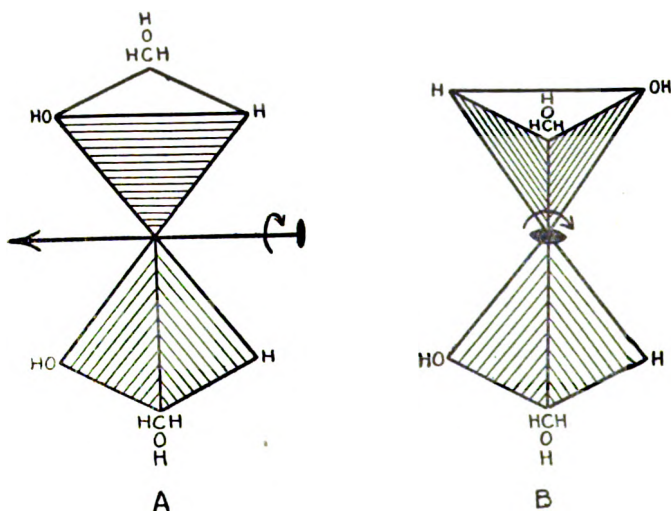
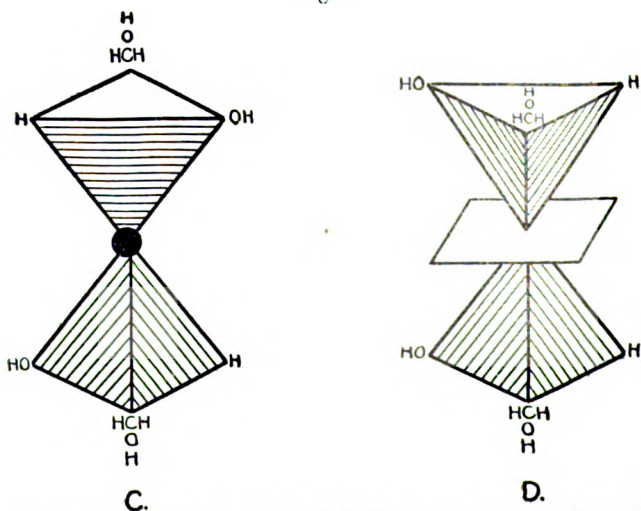


Fig. 2.



their mirror-images\* : A and B thus represent either *di-* or *l-*erythritol.

\* Cf. F. M. Jaeger, 'Lectures on the Principle of Symmetry and Its Applications in all Natural Sciences'; and also F. M. Jaeger, *Rec. Trav. Chim. des Pays-Bas*, xxxviii. p. 174, *et seq.* (1920).

On the other hand, C and D (D has been obtained from C in the same way as B from A) show symmetry of the second kind, viz. C a centre of symmetry, D a plane of symmetry. They are two possible representations of *i*-erythritol.

It is probable that the chemical molecule (the molecule as present in a solvent or in the gaseous state of a substance \*) has statistically the most symmetrical configuration which is consistent with its structure. The determination of the symmetry of the crystal-molecule (the molecule which is present in the crystal †) is often of use in deciding the nature of this "free" symmetry.

In general the crystal-molecule will be less symmetrical than the chemical-molecule, the distortion being due to forces brought into play by the act of the crystallization. It is, moreover, quite conceivable that a more or less symmetric chemical-molecule may lose all its symmetry as a consequence of this process. Therefore it is by no means certain that a definite symmetry element which may well be present in the "liquid" state will be found in the crystalline state. But it is fairly safe to assume that if a crystal-molecule proves to have a certain element of symmetry, that same element will be present in the chemical-molecule, perhaps accompanied by other symmetry elements. X-ray analysis of organic compounds reveals the fact that the symmetrical crystal-molecules very often show symmetry properties which could have been deduced as "possible" from the stereochemical configuration. This may be seen from a few examples:—

Benzene ‡, naphthalene §, and anthracene § have probably a centre of symmetry; the same holds for hexachlorbenzene ‡, hexabrombenzene ‡, and oxalic acid ||. Urea ‡ has two perpendicular planes of symmetry intersecting in a two-fold axis, while symmetrical di-methylurea ‡ has one plane of symmetry (monomethylurea ‡ is asymmetric). Hexamethylenetetramine \*\* shows all the symmetry properties of its stereochemical configuration. In these cases and in

\* Sir W. H. Bragg, "The Significance of Crystal Structure," J. Chem. Soc. cxi. p. 2766 (1922).

† *Loc. cit.*

‡ H. Mark, *Ber. d. Deutschen Chem. Ges.* lviii. p. 1820 (1924).

§ Sir W. H. Bragg and W. L. Bragg, 'X-Rays and Crystal Structure,' 4th Edition, p. 252.

|| H. Hoffmann und H. Mark, *Ztf. für Physik. Chem.* cxi. p. 321 (1924).

¶ H. W. Gonell und H. Mark, *Ztf. für Physik. Chem.* cviii. p. 181 (1923).

\*\* R. G. Dickinson, J. Am. Chem. Soc. xlv. p. 22 (1923).

many others the possible stereochemical symmetry has wholly or partly been retained in the crystal\*. The greater the number of symmetry elements of the chemical-molecule, the greater will be the probability that some at least of these elements will appear in the crystal-molecule.

*D*-Erythritol crystallizes in the tetragonal bipyramidal class †. It forms well-developed crystals, often of considerable size. The crystallographic data are given by Groth ‡ :—

$$a : c = 1 : 0.3762.$$

Two values are given for the density. They show a considerable difference, viz. 1.590 § and 1.450 ||. A re-determination by the suspension-method, using as liquid a mixture of carbon tetrachloride ( $\rho = 1.593$ ) and benzene ( $\rho = 0.88$ ), gave  $\rho = 1.441$ .

A small section of a crystal was used in this work. Its size was about  $6 \times 3 \times 0.8$  mm. A Bragg ionization spectrometer with a Coolidge X-ray bulb of molybdenum anticathode was used to measure the spacings, and also relative intensities of the different orders of a few principal planes. Also powder and rotation photographs were taken with copper rays.

The crystal-section was cut parallel to the *c*-axis. It was found that the plane of the surface exposed was neither the (100) nor the (110) plane. X-ray measurements showed that a prism-plane, making an angle of  $45^\circ$  with the plane of the section, had the same spacing as another prism-plane at a corresponding angle of  $8^\circ 8'$ , both angles being measured in the same direction. These two equally-spaced sets of planes must be symmetrically disposed about either the (100) or the (110) plane, and make an angle of  $1/2 \times (45^\circ - 8^\circ 8') = 18^\circ 26'$  with one of them. The (100) plane has been chosen here. The two prism-planes in the tetragonal system which make an angle of  $18^\circ 26'$  with the (100) plane are the (310) and the  $\bar{3}10$  plane. The plane of the crystal section itself makes an angle of  $26^\circ 34'$  with the (100) plane, and is therefore the (210) plane. If the (110) plane is

\* However, it should be noted that, *e. g.* in penta-erythritol (*cf.* note \*, p. 291) the crystal-molecule possesses a four-fold rotation axis, whereas from a stereochemical point of view a more tetrahedral arrangement would appear probable.

† For a confirmation by Laue-photographs, see H. Haga and F. M. Jaeger, *Proc. Roy. Acad. of Amsterdam*, xviii. p. 1352 (1916).

‡ 'Chemische Kristallographie,' iii. p. 240.

§ Lamv, *Ann. d. Ch.* (3) xxxv. p. 139.

|| Schröder, *Ber. d. Deutschen Chem. Ges.* xii. p. 562 (1879).

chosen instead of the (100), the indices of the planes (210) and (130) are interchanged.

The following spectrometer measurements of a number of planes of the crystal were made (Table I.). The value of

TABLE I.

Plane.	Spacing (Å.).		Remarks on relative intensities of successive orders.
	Observed.	Calculated.	
(100) ...	6.38	12.76	II. weak; IV. and VI. strong; VIII. > II. II. very strong; II. > IV. > VI. > VIII.
(110) ...	4.50	9.02	
(210) ...	2.86	5.71	
(310) ...	2.02	4.03	
(410) ...	1.55	3.09	
(510) ...	1.26	2.50	
(710) ...	*	1.81	
(320) ...	1.77	3.54	
(520) ...	1.18	2.37	
(430) ...	1.28	2.55	
(530) ...	1.09	2.19	
(730) ...	*	1.68	
(540) ...	1.00	1.99	IV. moderately strong; IV. >> VIII. I. and II. strong; II. > I. >> IV. > III.
(750) ...	*	1.48	
(970) ...	*	1.12	
(001) ...	1.71	6.83	II. strong; II. > IV.
(101) ...	6.03	6.02	
(301) ...	3.62 †	3.61	
(111) ...	2.73	5.44	
(211) ...	4.40	4.38	
(311) ...	1.74	3.47	
(321) ...	3.14 †	3.14	

\* Of these planes no reflexions could be found corresponding to the calculated spacings after careful examination. The second orders could not be found, obviously because the glancing angles became very large, viz.  $23^\circ$ ,  $25^\circ$ ,  $28\frac{1}{2}^\circ$ ,  $39\frac{1}{2}^\circ$  respectively.

† Calculated from a rotation photograph.

the spacing in the direction of the  $a$ -axis was determined by taking a rotation photograph with the  $a$ -axis as axis of rotation; it was found to be  $12.74 \text{ Å}$ . For the  $c$ -spacing was found in the same way  $6.80 \text{ Å}$ . From the spectrometer measurements can be deduced for these two spacings  $12.76 \text{ Å}$  and  $6.83 \text{ Å}$  respectively. The spacings of all planes in the table were calculated with the latter two values of  $a$  and  $c$ .

The spacing of the basal plane is quartered; all planes of the prism zone show halved spacings, and also those planes

( $hkl$ ) for which ( $h+k+l$ ) is odd. This was confirmed by a rotation photograph about the  $c$ -axis (Table II.).

TABLE II.

Indices of spots.	Obtained spacing in Å.	Calculated spacing in Å.
(220) .....	4.53	4.51
(420) .....	2.83	2.86
(440) .....	2.22	2.25
(101) .....	6.10	6.02
(211) .....	4.40	4.38
(301) .....	3.62	3.61
(321) .....	3.14	3.14
(112) .....	3.19	3.19
(202) .....	3.00	3.01
(222) .....	2.72	2.72
(332) } .....	2.23	{ 2.26
(422) }		{ 2.19

In the last two columns are given the spacings of the planes as obtained from the photograph and as calculated for a cell with  $a=12.76$  Å and  $c=6.83$  Å.

It should be noted that, while (222) was a very distinct spot, (111) was absent; (311) was also absent.

The observed quartering and halvings are in this class characteristic of the space-group  $C_{4h}^6$ , the fundamental lattice being the body-centred tetragonal lattice  $\Gamma_1^*$ .

From the above results the number of molecules per unit-cell is 8 (7.96).

As has been already stated, all measurements were made with a small crystal section, and the choice between the (100) and (110) planes was arbitrary. A well-developed crystal on which appeared the face described by Groth as (100) was examined on the spectrometer, and it was found that this plane corresponded to the (110) of the cell chosen above. This means that in the description used by Groth the crystal is referred to a face-centred lattice  $\Gamma_1'$ . In the tetragonal system this is geometrically equivalent to the body-centred lattice, which has been used in this investigation. The elementary parallelepiped has the same height in the two cases, but the side of the basal plane of the face-centred cell is the diagonal of the basal plane of the body-centred cell. It is easily seen that the necessary transforma-

\* W. T. Astbury and Kathleen Yardley, "Tabulated Data for the Examination of the 230 Space-groups by Homogeneous X-rays," *Phil. Trans. Roy. Soc. A*, ccxxiv. p. 239 (1924).

tion of the axial ratio used here (body-centred cell) reproduces that of Groth (face-centred cell).

The number of asymmetric bodies necessary for the construction of a body-centred unit-cell in the tetragonal bipyramidal class is 16; this means that sixteen asymmetric molecules can be disposed about the elements of symmetry in such a way that the symmetry of the whole is tetragonal bipyramidal. When, as in the present case, the cell contains only eight molecules, the molecules cannot be placed in the most general positions, but each molecule must occupy a special position in the unit-cell and possess two-fold symmetry of its own. The tables of Astbury and Yardley show that the possible molecular symmetry in this case is either a centre of symmetry or a two-fold axis. This conclusion can be easily deduced from a consideration of the diagram\* which represents this space-group, in the way described by the authors.

The arrangement of the molecules in the two cases can be seen from figs. 3 and 4, which represent projections

Fig. 3.

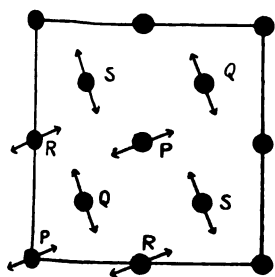
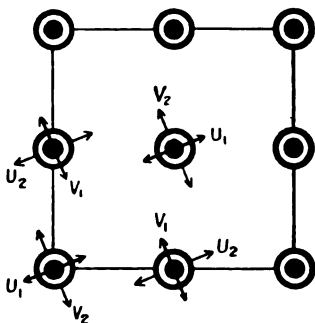


Fig. 4.



on the basal planes of the unit-cells. The positions in the unit-cells themselves are given in figs. 5 and 6.

When the eight molecules are centro-symmetrical (figs. 3 and 5), they are all completely identical in the sense that they can be obtained from each other without recourse to reflexions; *i.e.* they cannot be described as either right-handed or left-handed. For convenience we may consider them as four pairs, P, Q, R, S, each of these pairs being obtained from the preceding pair by a rotation about a tetragonal axis, followed by a translation of  $\frac{c}{4}$ .

\* *L. c.* p. 223 and Diagram No. 100.



5.

Hydrogen.

$\times 3.6$



6.

Hydrogen.

$\times 3.6$



7.

Hydrogen.

$\times 2.0$



8.

Helium.

22

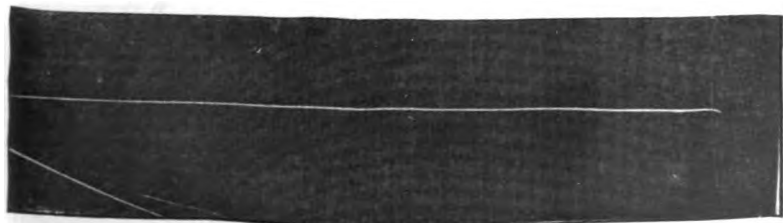


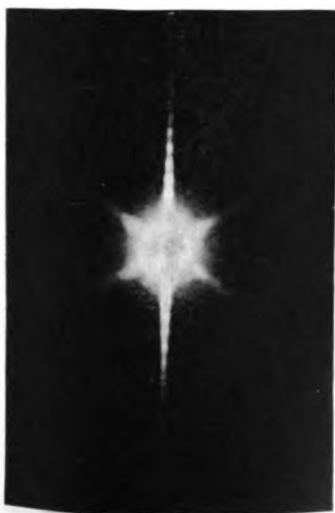




FIG. 2.



FIG. 3.





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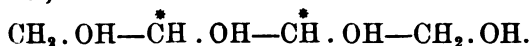
[SEVENTH SERIES.]

FEBRUARY 1926.

XXI. *An X-Ray Examination of i-Erythritol.*

By W. G. BURGERS (*Rockefeller Foundation Fellow*) \*.

THE present paper deals with the X-ray examination of an organic compound of relatively simple constitution, *i*-erythritol,



The investigation was undertaken mainly to determine the symmetry of the crystal-molecule. Erythritol is one of the simplest compounds with two so-called "asymmetric" carbon-atoms (indicated in the formula by asterisks), and moreover two which are linked with exactly similar groups of atoms. A difference in the spatial arrangement of these groups with regard to the "asymmetric" carbon-atoms is possible. This gives rise to the existence of a right-handed and a left-handed form, a racemic form, and an internally-compensated or meso form. The compound is wholly comparable with tartaric acid.

In figs. 1 and 2 the different forms are represented in the usual schematic way. The "asymmetric" carbon-atoms (which are not represented in the figures) occupy corresponding positions within the tetrahedra. According to the conventions of stereochemistry, the configurations in these figures are drawn in the most symmetrical way.

A and B are two possibilities of the same active form (B has been obtained from A by rotating the upper tetrahedron through 180° about the bond between the two

\* Communicated by Sir William Bragg, K.B.E., F.R.S.



asymmetric carbon-atoms). They have a two-fold axis as the only symmetry-element, and are therefore different from

Fig. 1.

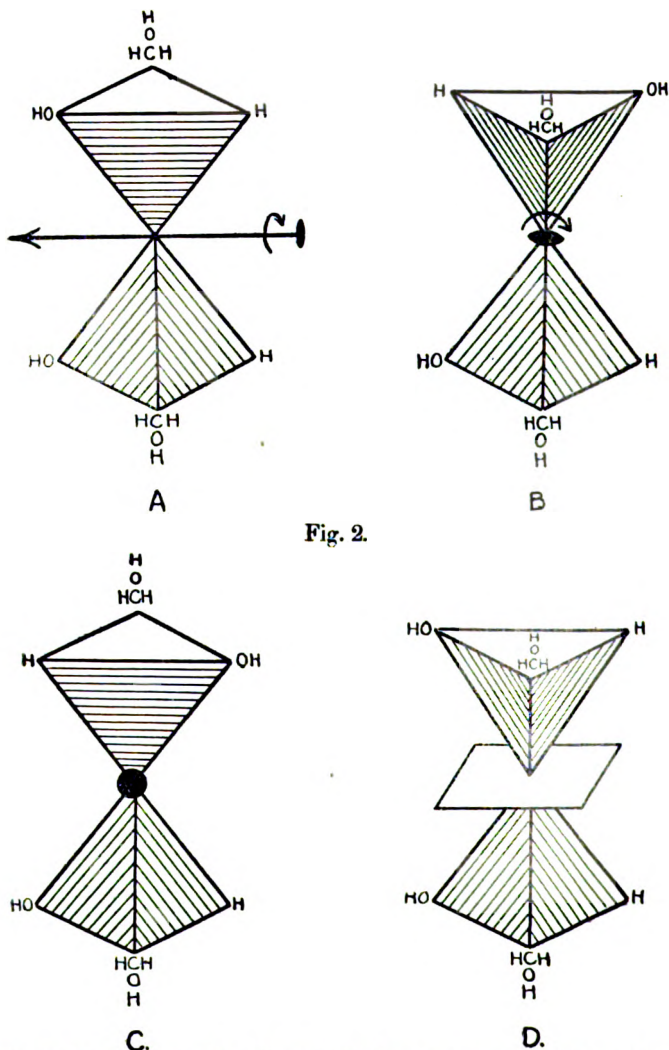


Fig. 2.

their mirror-images \* : A and B thus represent either *di*- or *L*-erythritol.

\* Cf. F. M. Jaeger, 'Lectures on the Principle of Symmetry and Its Applications in all Natural Sciences'; and also F. M. Jaeger, *Rec. Trav. Chim. des Pays-Bas*, xxxviii. p. 174, *et seq.* (1920).

On the other hand, C and D (D has been obtained from C in the same way as B from A) show symmetry of the second kind, viz. C a centre of symmetry, D a plane of symmetry. They are two possible representations of *i*-erythritol.

It is probable that the chemical molecule (the molecule as present in a solvent or in the gaseous state of a substance \*) has statistically the most symmetrical configuration which is consistent with its structure. The determination of the symmetry of the crystal-molecule (the molecule which is present in the crystal †) is often of use in deciding the nature of this "free" symmetry.

In general the crystal-molecule will be less symmetrical than the chemical-molecule, the distortion being due to forces brought into play by the act of the crystallization. It is, moreover, quite conceivable that a more or less symmetric chemical-molecule may lose all its symmetry as a consequence of this process. Therefore it is by no means certain that a definite symmetry element which may well be present in the "liquid" state will be found in the crystal-line state. But it is fairly safe to assume that if a crystal-molecule proves to have a certain element of symmetry, that same element will be present in the chemical-molecule, perhaps accompanied by other symmetry elements. X-ray analysis of organic compounds reveals the fact that the symmetrical crystal-molecules very often show symmetry properties which could have been deduced as "possible" from the stereochemical configuration. This may be seen from a few examples :—

Benzene ‡, naphthalene §, and anthracene § have probably a centre of symmetry; the same holds for hexachlorbenzene ‡, hexabrombenzene ‡, and oxalic acid ||. Urea ‡ has two perpendicular planes of symmetry intersecting in a two-fold axis, while symmetrical di-methylurea ‡ has one plane of symmetry (monomethylurea ‡ is asymmetric). Hexamethylenetetramine \*\* shows all the symmetry properties of its stereochemical configuration. In these cases and in

\* Sir W. H. Bragg, "The Significance of Crystal Structure," J. Chem. Soc. cxi. p. 2766 (1922).

† *Loc. cit.*

‡ H. Mark, *Ber. d. Deutschen Chem. Ges.* lvii. p. 1820 (1924).

§ Sir W. H. Bragg and W. L. Bragg, 'X-Rays and Crystal Structure,' 4th Edition, p. 252.

|| H. Hoffmann und H. Mark, *Ztf. für Physik. Chem.* cxi. p. 321 (1924).

¶ H. W. Gonell und H. Mark, *Ztf. für Physik. Chem.* cvii. p. 181 (1923).

\*\* R. G. Dickinson, J. Am. Chem. Soc. xlv. p. 22 (1923).



many others the possible stereochemical symmetry has wholly or partly been retained in the crystal\*. The greater the number of symmetry elements of the chemical-molecule, the greater will be the probability that some at least of these elements will appear in the crystal-molecule.

*i*-Erythritol crystallizes in the tetragonal bipyramidal class†. It forms well-developed crystals, often of considerable size. The crystallographic data are given by Groth‡ :—

$$a : c = 1 : 0.3762.$$

Two values are given for the density. They show a considerable difference, viz. 1.590§ and 1.450||. A re-determination by the suspension-method, using as liquid a mixture of carbon tetrachloride ( $\rho = 1.593$ ) and benzene ( $\rho = 0.88$ ), gave  $\rho = 1.441$ .

A small section of a crystal was used in this work. Its size was about  $6 \times 3 \times 0.8$  mm. A Bragg ionization spectrometer with a Coolidge X-ray bulb of molybdenum anticathode was used to measure the spacings, and also relative intensities of the different orders of a few principal planes. Also powder and rotation photographs were taken with copper rays.

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§ Lamv, *Ann. d. Ch.* (3) xxxv. p. 139.

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(750) ...	*	1.48	
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(001) ...	1.71	6.83	IV. moderately strong; IV. > VIII.
(101) ...	6.03	6.02	I. and II. strong; II. > I. > IV. > III.
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the spacing in the direction of the  $a$ -axis was determined by taking a rotation photograph with the  $a$ -axis as axis of rotation; it was found to be 12.74 Å. For the  $c$ -spacing was found in the same way 6.80 Å. From the spectrometer measurements can be deduced for these two spacings 12.76 Å and 6.83 Å respectively. The spacings of all planes in the table were calculated with the latter two values of  $a$  and  $c$ .

The spacing of the basal plane is quartered; all planes of the prism zone show halved spacings, and also those planes

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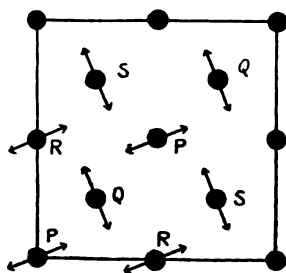
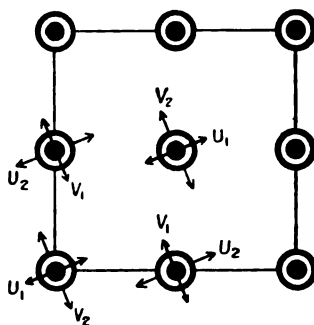


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\* *L. c.* p. 223 and Diagram No. 100.

In the other case (figs. 4 and 6) four of the molecules, viz. two  $U_1$  and two  $V_1$ , are the mirror images of the other four, viz. two  $U_2$  and two  $V_2$ . A  $U_1$ -molecule may be obtained from a  $V_1$ -molecule by a rotation of  $90^\circ$  about a tetragonal axis, followed by a translation of  $\frac{c}{4}$ ; the same relation holds for  $U_2$  and  $V_2$ .

Fig. 5.

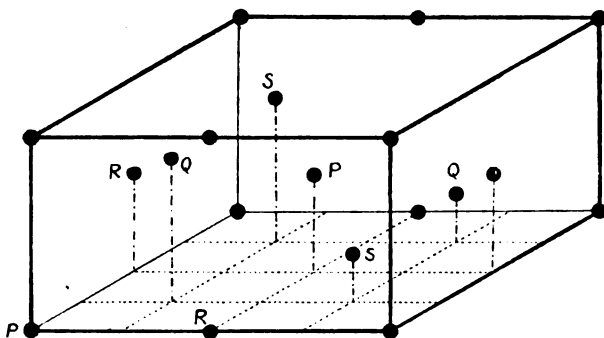
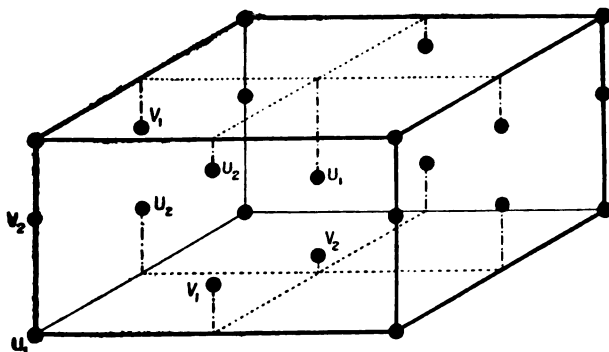


Fig. 6.



The directions of the arrows represent diagrammatically the difference in orientation of the molecules as a consequence of the above-mentioned rotation.

In both cases definite points of the molecules, viz. corresponding points of the two-fold axes of the axially-symmetric molecules and the symmetry-centres of the centrosymmetric molecules, occupy eight equivalent positions in the unit-cell. The coordinates of these positions referred to the edges of the unit-cell can be deduced from the diagram

mentioned above; or they can be found in R. W. G. Wyckoff's 'The Analytical Expression of the Results of the Theory of Space-Groups' \*.

When the unit-cells are chosen in such a way that the corners are occupied by molecules, then the coordinates of the 8 centres of the centro-symmetrical molecules are:

$$\begin{aligned} 0\ 0\ 0; & \frac{1}{4}\ \frac{1}{4}\ \frac{3}{4}; \frac{1}{2}\ 0\ \frac{1}{2}; \frac{3}{4}\ \frac{1}{4}\ \frac{3}{4} \\ 0\ \frac{1}{2}\ 0; & \frac{1}{4}\ \frac{3}{4}\ \frac{1}{4}; \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}; \frac{3}{4}\ \frac{3}{4}\ \frac{1}{4}, \end{aligned}$$

and the coordinates of the 8 equivalent points of the axially-symmetric molecules are:

$$\begin{aligned} 0\ 0\ 0; & \frac{1}{2}\ 0\ \frac{3}{4}; 0\ \frac{1}{2}\ \frac{1}{4}; \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2} \\ 0\ 0(\frac{3}{4}-2u); & \frac{1}{2}\ 0(\frac{1}{2}-2u); \quad 0\ \frac{1}{2}\ \overline{2u}; \frac{1}{2}\ \frac{1}{2}(\frac{1}{4}-2u). \end{aligned}$$

It can be seen at once, that while the centres of the centro-symmetric molecules are placed in quite definite positions, one degree of freedom with regard to their positions on the *c*-axis remains for the axially-symmetric molecules.

It is not possible to decide between these two possibilities with such a certainty as accompanies the determination of the space-group and the number of molecules in the unit-cell. However, a consideration of the intensities of the reflexions of a few principal planes, and also of the external form of the crystal, gives strong evidence of the presence of a centre of symmetry in the crystal-molecule.

In what follows the presence of centro-symmetric molecules is indicated as case *a*, the presence of axially-symmetric molecules as case *b*.

The principal planes have the longest spacings, and, as a consequence, the molecules have the largest distance from each other in directions perpendicular to these planes; therefore, in making an approximation of the reflexion intensities of these special planes, it is justifiable in the first instance to consider each molecule as a single scattering centre, at least for the first orders. For the higher orders, and for the reflexions of more complicated planes it is, in most cases, not possible to interpret even roughly the intensities in such a simple way.

In Table III. the approximate relative intensities from successive orders of three planes are given, as found by spectrometer measurements.

The actual numbers given are average values for different observations, and must be considered only as giving a general

\* Carnegie Institution of Washington, Publication No. 318.

TABLE III.

Plane.	Approximate relative intensities from successive orders.							
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
(100) ... ..	...	10	...	65	...	120	...	17
(110) .....	...	400	...	90	...	10	...	5
(101) .....	130	160	3	10				

idea of the relative magnitudes of the reflexions. But the conclusions drawn from them and summed up in the following points are beyond any doubt, viz. :—

1. By far the strongest reflexion is given by (110), much stronger than by (100).
2. The IInd order of (100) is very weak, the IVth and VIth orders are strong, the VIIIth order is stronger than the IInd.
3. The (101) plane gives strong Ist and IInd orders, the IIIrd order is very weak, the IVth order stronger than the IIIrd.

The two possible arrangements of the molecules with regard to the main prism-planes (100) and (110) can be easily seen in figs. 3 and 4. They show obviously that the experimental results (1) and (2) are in general agreement with fig. 3, *i. e.* case *a*. Indeed, in fig. 3 the (110) plane is more closely packed with molecules than the (100) plane, while in fig. 4 the converse is true. So in case *a* we expect (110) to be the stronger reflecting plane; in case *b*, on the contrary, (100).

And further, in fig. 3, the (100) planes which carry P and R molecules are half-way interleaved by planes carrying Q and S molecules; a similar arrangement does not occur in fig. 4. Therefore, in case *a* a weak IInd order and a strong IVth order can be expected, and are actually found. The VIth order is also very strong, and although this may seem to be strange, it is not necessarily contradictory to the conclusions already drawn. In fact, since the molecules are in reality groups of scattering atoms, and are, moreover, differently orientated with regard to the successive (100) planes, it is quite possible that, although certain atoms of the Q and S molecules will weaken the rays scattered by certain

atoms of the P and R molecules in both the II<sup>nd</sup> and the VI<sup>th</sup> orders of (100), other atoms will reinforce each other in the VI<sup>th</sup> order only. If there were no difference in orientation between P and R molecules on the one hand, and Q and S molecules on the other, the VI<sup>th</sup> order would be quite absent together with the II<sup>nd</sup> order, *i. e.* (100) would be quartered. However, as has already been stated, there is a difference in orientation, caused by a rotation about a tetragonal axis, and this difference will, in general, have its greatest effect on the reflexions of the prism-planes. It will be of less importance for the (101) plane, which makes, on account of the small axial ratio, an angle of only  $28^{\circ} 9'$  with (001), and actually for this plane the agreement between calculated and observed intensities proves to be better for the higher orders. With regard to the (001) plane itself, P, Q, R, and S molecules are identical: the plane is really quartered.

The distribution of the molecules with regard to the (101) plane can be found by substituting the values of the co-ordinates of the 8 equivalent points in the equation of a plane:

$$hx + ky + lz = p,$$

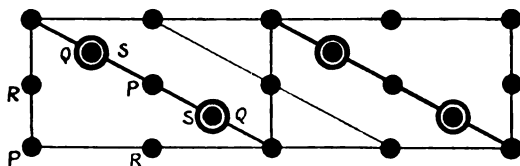
in which  $x, y, z$  are the coordinates of one of its points, expressed in fractions of the edges of the unit-cell, and  $h, k, l$  the indices of the plane\*. When this is done for the 8 centres,  $p$  takes the values:

$$(a) \quad 0, 0, 1, \frac{1}{2}, 1, 1, 1\frac{1}{2}, 1.$$

In case  $b$  we get:

$$(b) \quad 0, \frac{3}{4} - 2u, 1\frac{1}{4}, 1 - 2u, \frac{1}{4}, -2u, 1, \frac{3}{4} - 2u.$$

Fig. 7.



$\alpha$  implies that the centres of the centro-symmetric molecules are located in two sets of (101) planes, the one set interleaving half-way the other set, and the planes contain alternately numbers of molecules in the ratio 6:2. This can also be seen in fig. 7, which represents a projection of the

\* Cf. W. T. Astbury, "The Crystalline Structure of Anhydrous Racemic Acid," Proc. Roy. Soc. A, civ. p. 224.



unit-cell on a (100) plane. If again we consider the molecules as single scattering-centres, we can get a rough approximation of the intensities of the different orders of reflexion for the (101) plane by using the formula \*

$$J \sim A^2 \frac{1 + \cos^2 2\theta}{n^2},$$

in which  $\theta$  and  $n$  have their usual meaning and  $A$  is the amplitude of the scattered rays.  $A$  is proportional to  $(6-2)$  in the odd orders, and to  $(6+2)$  in the even orders. The angle  $\theta$  for the 1st order is  $3^\circ 22'$ .

Substituting these values, we get :

$$J_1 \sim \frac{(6-2)^2}{1^2} \times 1.99, \quad \text{i.e.} \quad J_1 \sim 32,$$

$$J_2 \sim \frac{(6+2)^2}{2^2} \times 1.95, \quad \text{i.e.} \quad J_2 \sim 31,$$

$$J_3 \sim \frac{(6-2)^2}{3^2} \times 1.88, \quad \text{i.e.} \quad J_3 \sim 3.3,$$

$$J_4 \sim \frac{(6+2)^2}{4^2} \times 1.80, \quad \text{i.e.} \quad J_4 \sim 7.2.$$

These numbers are in general agreement with the figures in the table, in so far that the 1st and IIInd order are strong, compared with the very weak IIIrd order, and that the IVth order is stronger than the IIInd.

In case  $b$  we have to take into consideration the different values of  $u$ ; it is, however, easy to see that, assuming the same simplifications as before, for all values of  $u$  a weak IIInd order for (101) would be expected. From the series

$$0, \frac{1}{4}; 1, 1\frac{1}{4}; -2u, \frac{3}{4} - 2u; 1 - 2u, \frac{3}{4} - 2u,$$

we see that for every molecule lying in a given (101) plane there is always a corresponding molecule lying in a plane removed from it by a distance  $\frac{1}{4}d_{(101)}$ ; i.e. the rays reflected by any two such corresponding molecules are opposite in phase, and the IIInd order is weak, in striking contrast with the experimental value, which shows the IIInd order to be the strongest.

A consideration of the habit of the crystal is of importance because the best faces developed are generally the most closely packed with molecules†. According to Groth, crys-

\* Cf. R. W. G. Wyckoff, 'The Structure of Crystals,' p. 102 (1924); also Sir W. H. Bragg and W. L. Bragg, 'X-rays and Crystal Structure,' pp. 114, 131, 206.

† Cf. W. T. Astbury, *l.c.* p. 225.

tals of *i-erythritol* show the following faces:—(100), (111), (131), (311). It is further stated that, besides (100), sometimes (111) is very large, sometimes (131). In the Davy-Faraday laboratory are splendid crystals of this substance, some of them measuring several *inches* across. They showed the same faces as given by Groth. (100, (111), and (131) were mostly very large, especially the first two; (311) was usually smaller. But besides these faces (110) was often present, always, however, very much smaller than (100). A few crystals showed (331) as a very small face. No other faces were found on these crystals.

Transforming the indices of these six planes, viz. (100), (111), (131) and (311), (110), (331), (face-centred cell) to the indices required of the body-centred cell which we have chosen, we obtain :

(110), (101), (211) and (121), (100), (301).

The numbers of molecules per unit-surface ( $\sigma$ ) for different planes can be compared by determining for each plane the distance  $d_1$  between successive planes which are equally packed with molecules. Indeed,  $\frac{\sigma}{d_1}$  represents the number of molecules per unit-volume \*, and is therefore a constant for the crystal. So we see that  $\sigma$  is proportional to  $d_1$ , and we can compare the molecular densities of different faces by comparing the spacings of equally packed planes parallel to them.

The spacings  $d_1$  are either equal to the true spacings  $d$  (which are the distances between planes identical both with regard to the number of molecules as to the orientation of these molecules) or a sub-multiple of them.

The sub-multiple for each plane is found by substituting the coordinates of the eight equivalent points in the equation  $hx + ky + lz = p$  of the plane, as has already been done for (101). We find in case *a* (centro-symmetrical molecules) that the planes which correspond to the true periodicity are interleaved by one or three parallel planes, also carrying molecules. Thus in those cases where successive planes are equally packed with molecules, the sub-multiple is clearly  $\frac{1}{2}$  or  $\frac{1}{4}$ .

However, there are faces, *e.g.* (101), successive planes of which carry numbers of molecules in the ratio 3:1. With regard to these faces, equally packed planes have the true spacing  $d$ , but, the number of molecules in one series of

\* See *e.g.*, P. P. Ewald, 'Kristalle und Röntgenstrahlen,' p. 26.

them being  $\frac{1}{4}$  of all the molecules, the molecular-density  $\sigma$  is measured by  $\frac{1}{4}$  of the spacing  $d$ .

In Table IV. a number of planes are tabulated according to decreasing spacings  $d$  (true spacing). The first column gives the indices of the planes (as used in our description), the second column  $d$ .

TABLE IV.

Plane.	$d$ .	Centro-sym. molecules.		Axially-sym. molecules.	
		Sub-multiple number.	$d_1$ .	Sub-multiple number.	$d_1$ .
(100) .....	12.76	4	3.19	2	6.38
(110) .....	9.02	2	4.51	2	4.51
(001) .....	6.83	4	1.71	8	0.86
(101) .....	6.02	2*	4.51	4	1.50
(210) .....	5.72	4	1.43	2	2.86
(111) .....	5.44	4	1.36	8	0.68
(201) .....	4.66	4	1.17	8	0.58
(121) .....	4.38	2*	3.28	4	1.10
(310) .....	4.00	2	2.00	2	2.00
(221) .....	3.76	4	0.94	8	0.47
(301) .....	3.61	2*	2.71	4	0.90
(320) .....	3.54	4	0.89	2	1.77
(311) .....	3.47	4	0.87	8	0.43
(102) .....	3.30	4	0.82	4	0.82
(112) .....	3.19	2	1.59	2	1.59
(321) .....	3.14	2*	2.36	4	0.78
(410) .....	3.10	4	0.77	2	1.55
(122) .....	2.93	4	0.73	4	0.73

The third and fourth column refer to case *a*.

The numbers in the third column (sub-multiple numbers) indicate that the true spacings for the planes in question are "halved" or "quartered" by equally packed parallel planes; 2\* indicates the special case mentioned, when the ratio of the numbers of molecules for successive planes is 3:1. The fourth column contains the "reduced" spacings  $d_1$ . The numbers in this column are proportional to the molecular-densities of the respective planes. When we arrange these numbers in order of magnitude, we obtain :

4.51 ; 4.51 ; 3.28 ; 3.19 ; 2.71 ; and so on,  
corresponding to the faces :

(110), (101), (121) and (211), (100), (301), etc.

These are just the faces shown by the crystals.

A similar calculation can be made for case *b*. In the fifth and sixth columns of Table IV. are given the sub-multiple numbers and the "reduced" spacing  $d_1$ , calculated when no

special value is chosen for  $u$ . The agreement between the numbers  $d_1$  and the actual faces of the crystal, which was obtained in case  $a$ , is in no way present in this case. It is possible by giving special values to  $u$ , e. g.  $\frac{1}{8}$ , to increase  $d_1$  for several planes, but this does not influence the prism-faces. For all values of  $u$  (100) is closer packed than (110), while the crystal shows always (110) as a far better developed plane than (100). Likewise for all values of  $u$  (100) is closer packed than (101), and (210) closer packed than (121); the face (210) was not present on any of the crystals.

So the habit of the crystal is in perfect agreement with the hypothesis of centro-symmetric crystal-molecules of *i*-erythritol. The fact that there is often a difference in the development of the two faces (211) and (121) must be caused by the difference in orientation of the molecules with regard to these two planes, because the density of molecule-centres is the same for both. It was also observed that there was a marked difference between the reflexions from these two planes. The plane which has the stronger 1st order has the weaker 2nd order.

#### SUMMARY.

It is shown that the space-group of *i*-erythritol, which crystallizes in the tetragonal-bipyramidal class, is  $C_{4h}^6$ .

The body-centred unit-cell ( $\Gamma_1'$ ) contains eight molecules. The crystal-molecule must possess two-fold symmetry, either a centre or a two-fold axis. It is concluded that the crystal-molecule is centro-symmetrical, and the reasons are given on which this conclusion is based.

A crystallographic confirmation is thus given to the configuration of *i*-erythritol already assigned by stereochemistry.

The author wishes to give expression to his great indebtedness to the President and Officers of the International Education Board of the Rockefeller Foundation for the grant of a science fellowship which made this research possible, and to thank sincerely Sir William Bragg for his kindness and the hospitality received in the Davy-Faraday Research Laboratory.

In conclusion, he wishes to thank Prof. Dr. F. M. Jaeger, at Groningen (Holland), for the kind loan of the crystal-section used in the investigation, and Mr. W. T. Astbury for his much appreciated advice and help.

London, June 19, 1925.

**XXII. On certain Functions of Two Variables and their Integrals related to the Bessel Coefficients.** By E. T. BELL\*.

1. *THE FUNCTIONS L.*—Throughout the paper  $n \geq 0$  is an integer;  $\lambda, \mu, \nu, \rho, z, y$  are variables; and the  $\epsilon_n$  are Neumann's factors,  $\epsilon_0 = 1, \epsilon_{n+1} = 2$ .

The function  $L(\lambda, \mu)$  is defined by the absolutely convergent series for all finite  $\lambda, \mu$ :

$$L_n(\lambda, \mu) = \frac{1}{2}n! \sum_0^\infty \frac{\lambda^{n+j}\mu^j}{j!(n+j)!}, \quad \dots \quad (1)$$

and we have

$$2L_n(\lambda, \mu) = n! \epsilon_n A_n(\lambda, \mu),$$

where

$$\exp(\lambda t + \mu t^{-1}) = A_0 + \sum_1^\infty (A_r t^r + B_r t^{-r}),$$

with

$$A_n \equiv A_n(\lambda, \mu), \quad B_n \equiv B_n(\lambda, \mu),$$

these being the functions of Spitzer †.

The introduction of the factor  $\frac{1}{2}n! \epsilon_n$  in (1) is an essential modification. It greatly simplifies the algebraic details of the entire subject, and makes possible the use of an extremely simple symbolic method, explained in § 2, which otherwise is not practicable. The proofs of (20), (21) below illustrate as well as any others the gain in algebraic simplicity.

It follows from the definition (1), or immediately as in § 3, that

$$L_n(\lambda, -\mu) = \frac{1}{2}n! \epsilon_n (\sqrt{\lambda/\mu})^n J_n(2\sqrt{\lambda\mu}), \quad \dots \quad (2)$$

$$L_n\left(\frac{z}{2}, -\frac{z}{2}\right) = \frac{1}{2}n! \epsilon_n J_n(z), \quad \dots \quad (3)$$

where  $J_n(z)$  is the Bessel coefficient of order  $n$ . See also (12).

All of the information used here concerning  $J_n(z)$  is available in chapter 2 of Watson's 'Theory of Bessel Functions' (1923) or in the 'Bessel Functions' of Gray, Mathews, and MacRobert (1922). From (2), (3) it follows that any formula for functions  $L_n(\lambda, \mu)$  contains as a special case one for  $J_n(z)$ . The introduction of the factor  $\frac{1}{2}n! \epsilon_n$

\* Communicated by the Author.

† *Archiv für Math. u. Physik*, vol. iii. pp. 244-46 (1859).

thus enables us to apply the simple symbolic method to the Bessel coefficients. Many of the important integrals evaluated in terms of Bessel coefficients appear as degenerate forms (one variable equal to a constant) of integrals expressible as functions  $L_n(\lambda, \mu)$ . A short selection is given in §§ 8, 9.

2. *Umbral Notation.*—The umbra  $\alpha$  is taken as the representative of the entire class of ordinary quantities, or *ordinaries*,  $\alpha_n$  ( $n=0, 1, \dots$ ), and  $\alpha_n$  is written  $\alpha$  until after the completion of all algebraic operations, when exponents are degraded to suffixes. Umbral powers  $\alpha^n, \beta^n$  are manipulated as if they were ordinaries; thus, for example,

$$\alpha^m \cdot \alpha^n = \alpha^{m+n} = \alpha_{m+n}.$$

For  $z$  an ordinary,  $\alpha$  an umbra, the umbral exponential function is

$$\exp \alpha z \equiv e^{\alpha z} \equiv \sum_0^\infty \alpha^n z^n / n! \equiv \sum \alpha_n z^n / n!; \quad \dots \quad (4)$$

the umbral binomial theorem is

$$(\alpha + \beta)^n \equiv \sum_0^n \binom{n}{r} \alpha^{n-r} \beta^r \equiv \sum^n \binom{n}{r} \alpha_{n-r} \beta_r, \quad (\alpha + \beta)^0 = \alpha_0 \beta_0, \quad (5)$$

and hence

$$\exp \alpha z \cdot \exp \beta z = \exp (\alpha + \beta) z \quad \dots \quad (6)$$

The umbral or representative notation is due to Blissard.

3. *Expansions.*—The Laurent expansion of the left of (6.1) is valid for all  $t \neq 0$ . Assume that the expansion can be written in the form indicated, where  $\phi_n, \psi_n$  are to be replaced by  $\phi_n, \psi_n$  after expansion of the umbral exponentials,

$$\exp (\lambda t + \mu t^{-1}) = \exp \phi(\lambda, \mu) t + \exp \psi(\lambda, \mu) t^{-1}. \quad \dots \quad (6.1)$$

Replace by  $t^{-1}$ ; then

$$\phi(\lambda, \mu) = \psi(\mu, \lambda).$$

Compare with Spitzer's expansion in § 1 and (1); then

$$\exp (\lambda t + \mu t^{-1}) = \exp L(\lambda, \mu) t + \exp L(\mu, \lambda) t^{-1}. \quad \dots \quad (7)$$

From (7) and

$$\exp \frac{z}{2} (t - t^{-1}) = J_0(z) + \sum_1^\infty \{t^r + (-1)^r t^{-r}\} J_r(z)$$

we get (3), and from (7), with  $z, t$  replaced by  $2\sqrt{\lambda\mu}, t\sqrt{\lambda/\mu}$  respectively, we see (2).

In (7) replace  $t$  by  $\mu t$  or by  $t/\lambda$  and compare with (7) :

$$\mu^n L_n(\lambda, \mu) = \lambda^n L_n(\mu, \lambda) = L_n(\lambda\mu, 1) = \mu^n \lambda^n L_n(1, \mu\lambda), \quad (8)$$

and therefore (7) can be written

$$\exp(\lambda t + \mu t^{-1}) = \exp L(\lambda, \mu)t + \exp \lambda^{-1} \mu L(\lambda, \mu)t^{-1}, \quad (9)$$

or, what is the same,

$$\exp(\lambda t + \mu t^{-1}) = \sum_0^\infty \frac{L_n(\lambda, \mu)}{n!} \left[ t^n + \frac{\mu^n}{\lambda^n t^n} \right], \quad (10)$$

and hence by (2),

$$\begin{aligned} \exp(\lambda t - \mu t^{-1}) &= \frac{1}{2} \sum \epsilon_n (\sqrt{\lambda/\mu}) J_n(2\sqrt{\lambda\mu}) [t^n + (-\mu/\lambda)^n t^{-n}]. \end{aligned} \quad (11)$$

In connexion with the integrals, the following, evident from (2) or (11), is important :

$$L_n\left(\frac{y+z}{2}, \frac{y-z}{2}\right) = \frac{n!}{2} \epsilon_n \left( \sqrt{\frac{z+y}{z-y}} \right)^n J_n(\sqrt{z^2 - y^2}). \quad (12)$$

4. *Derivatives.*—Write

$$\frac{\partial}{\partial \lambda} L_n(\lambda, \mu) \equiv L_{n\lambda}(\lambda, \mu) \equiv L_{\lambda^n}(\lambda, \mu),$$

the last being umbral. The derivatives with respect to  $\lambda, \mu$  of (7) upon reduction by (7) give at once

$$\begin{aligned} & t[\exp L(\lambda, \mu)t + \exp L(\mu, \lambda)t^{-1}] \\ &= \exp L_\lambda(\lambda, \mu)t + \exp L_\mu(\mu, \lambda)t^{-1}, \\ & t^{-1}[\exp L(\lambda, \mu)t + \exp L(\mu, \lambda)t^{-1}] \\ &= \exp L_\mu(\lambda, \mu)t + \exp L_\lambda(\mu, \lambda)t^{-1}. \end{aligned}$$

Equating coefficients of like powers of  $t$ , and observing (8), we get

$$\left. \begin{aligned} \frac{\partial}{\partial \lambda} L_0(\lambda, \mu) &= \frac{\mu}{2\lambda} L_1(\lambda, \mu), \\ \frac{\partial}{\partial \mu} L_0(\lambda, \mu) &= \frac{1}{2} L_1(\lambda, \mu), \\ \frac{\partial}{\partial \lambda} L_1(\lambda, \mu) &= 2L_0(\lambda, \mu), \\ \frac{\partial}{\partial \mu} L_{n+1}(\lambda, \mu) &= \frac{1}{n+2} L_{n+2}(\lambda, \mu), \\ \frac{\partial}{\partial \lambda} L_{n+2}(\lambda, \mu) &= (n+2) L_{n+1}(\lambda, \mu). \end{aligned} \right\} \quad (13)$$

These can be verified by (1).

5. Recurrences.—Write

$$L_n \equiv L_n(\lambda, \mu), \quad M_n \equiv L_n(\mu, \lambda).$$

Differentiate (7) with respect to  $t$  and get

$$[(\lambda - L)t^2 - \mu] \exp Lt + [\lambda t^2 - (\mu - M)] \exp Mt^{-1} = 0.$$

The result of equating to zero the several powers of  $t$  is

$$\mu L_2(\lambda, \mu) + 2L_1(\lambda, \mu) - 4\lambda L_0(\lambda, \mu) = 0, \quad . \quad . \quad (14)$$

$$\mu L_{n+3}(\lambda, \mu) + (n+3)(n+2) [L_{n+2}(\lambda, \mu) - \lambda L_{n+1}(\lambda, \mu)] = 0, \quad . \quad (15)$$

which enable us to compute the functions  $L_n$  successively from  $L_0, L_1$ . For  $2\lambda = -2\mu = z$  these give as a check the recurrence for  $J_n(z)$ .

6. Differential Equations.—Write  $y \equiv L_n(\lambda, \mu)$ . Then an easy reduction by (13), (14), (15) gives immediately

$$\frac{\partial^2 y}{\partial \lambda \partial \mu} = y, \quad . \quad . \quad . \quad (16)$$

$$\lambda \frac{\partial y}{\partial \lambda} - \mu \frac{\partial y}{\partial \mu} = ny, \quad . \quad . \quad . \quad (17)$$

and therefore by differentiation of (17),

$$\lambda \frac{\partial^2 y}{\partial \lambda^2} - (n-1) \frac{\partial y}{\partial \lambda} - \mu y = 0, \quad . \quad . \quad . \quad (18)$$

$$\mu \frac{\partial^2 y}{\partial \mu^2} + (n+1) \frac{\partial y}{\partial \mu} - \lambda y = 0, \quad . \quad . \quad . \quad (19)$$

the last two of which for  $2\lambda = -2\mu = z$  reduce to Bessel's equation for  $J_n(z)$ .

7. Addition Theorem.—If  $\alpha, \beta$  are any umbræ we have from (1) the definition, provided the series be convergent,

$$L_n(\alpha, \beta) \equiv \frac{n!}{2} \epsilon_n \sum_0^\infty \frac{\alpha_{n+j} \beta_j}{j! (n+j)!}.$$

By means of  $L$  functions whose arguments are umbræ, the addition theorem can be given the remarkably concise finite form:

$$L_n(\lambda + \nu, \mu + \rho) = [L(\lambda, \mu) + L(\nu, \rho)]^n + L_n[L(\lambda, \mu), L(\rho, \nu)] + L_n[L(\nu, \rho), L(\mu, \lambda)]. \quad (20)$$

The proof is immediate. In (7) replace  $\lambda, \mu$  by  $\nu, \rho$  respectively, multiply member by member the identity so



obtained by (7), use (6) to reduce the left, multiply out the product on the right, apply (6), (7) to the result, and equate coefficients of  $t^n$ .

Without the use of umbræ we have from (20),

$$\begin{aligned} L_n(\lambda + \nu, \mu + \rho) &= \sum_0^n \binom{n}{r} L_{n-r}(\lambda, \mu) L_r(\nu, \rho) \\ &+ \frac{n!}{2} \epsilon_n \sum_0^\infty \frac{1}{j! (n+j)!} [L_{n+j}(\lambda, \mu) L_j(\rho, \nu) \\ &+ L_{n+j}(\nu, \rho) L_j(\mu, \lambda)], \quad . . . . . (21) \end{aligned}$$

which by (3), with  $2\lambda = -2\mu = z$ ,  $2\nu = -2\rho = w$ , gives the usual addition theorem for  $J_n(z+w)$ . Neither  $J_n$  nor Spitzer's  $A_n$  has a finite (umbral) addition theorem like (20), owing to the lack of the factor  $n!$

8. *Integrals.*—A great variety of integrals can be evaluated by means of the  $L$  functions; a few illustrations must suffice here. In (10) replace  $t$  by  $\exp i\theta$ , equate reals and imaginaries in the result, and put  $\lambda + \mu = y$ ,  $\lambda - \mu = z$ :

$$\begin{aligned} e^{y \cos \theta} \cos(z \sin \theta) \\ = \sum_0^\infty \left[ 1 + \left( \frac{y-z}{y+z} \right)^n \right] L_n \left( \frac{y+z}{2}, \frac{y-z}{2} \right) \frac{\cos n\theta}{n!}, \quad (22) \end{aligned}$$

$$\begin{aligned} e^{y \sin \theta} \sin(z \sin \theta) \\ = \sum_0^\infty \left[ 1 - \left( \frac{y-z}{y+z} \right)^n \right] L_n \left( \frac{y+z}{2}, \frac{y-z}{2} \right) \frac{\sin n\theta}{n!}. \quad (23) \end{aligned}$$

To express these in terms of Bessel coefficients, we write

$$\begin{aligned} \frac{1}{2} \epsilon_n \left[ \left( \frac{z+y}{z-y} \right)^{n/2} + (-1)^n \left( \frac{z-y}{z+y} \right)^{n/2} \right] J_n(\sqrt{z^2 - y^2}) &\equiv R_n(y, z), \\ \frac{1}{2} \epsilon_n \left[ \left( \frac{z+y}{z-y} \right)^{n/2} - (-1)^n \left( \frac{z-y}{z+y} \right)^{n/2} \right] J_n(\sqrt{z^2 - y^2}) &\equiv S_n(y, z), \end{aligned}$$

and refer to (12), whence

$$e^{y \cos \theta} \cos(z \sin \theta) = \sum_0^\infty R_n(y, z) \cos n\theta, \quad (24)$$

$$e^{y \cos \theta} \sin(z \sin \theta) = \sum_0^\infty S_n(y, z) \sin n\theta. \quad (25)$$

Henceforth a summation without indicated limits refers to  $n=0$  to  $\infty$ , and we shall write when convenient

$$R_n(y, z) \equiv R_n, \quad S_n(y, z) \equiv S_n.$$

Multiply (24), (25) throughout by  $\cos n\theta$ ,  $\sin n\theta$  respectively, and integrate from 0 to  $\pi$  :

$$\epsilon_n \int_0^\pi e^{y \cos \theta} \cos(z \sin \theta) \cos n\theta d\theta = \pi R_n, \quad . \quad . \quad (26)$$

$$2 \int_0^\pi e^{y \cos \theta} \sin(z \sin \theta) \sin n\theta d\theta = \pi S_n, \quad . \quad . \quad (27)$$

and therefore by addition and subtraction,

$$2\epsilon_n \int_0^\pi e^{y \cos \theta} \cos(z \sin \mp n\theta) d\theta = \pi(2R_n \pm \epsilon_n S_n). \quad (28)$$

For  $n=0$  this becomes Parseval's integral,

$$\int_0^\pi e^{y \cos \theta} \cos(z \sin \theta) d\theta = \pi J_0(\sqrt{z^2 - y^2}); \quad (28.1)$$

while for  $r > 0$  (28) gives

$$\int_0^\pi e^{y \cos \theta} \cos(z \sin - r\theta) d\theta = \pi \left( \frac{z-y}{z+y} \right)^{r/2} J_r(\sqrt{z^2 - y^2}), \quad . \quad . \quad (28.2)$$

which for  $y=0$  is Bessel's integral, and

$$\int_0^\pi e^{y \cos \theta} \cos(z \sin + r\theta) d\theta = (-1)^r \pi \left( \frac{z-y}{z+y} \right)^{r/2} J_r(\sqrt{z^2 - y^2}). \quad . \quad . \quad (28.3)$$

Take the  $r$ th derivatives ( $r > 0$ ) with respect to  $y$ ,  $z$  of (26), (27) :

$$\epsilon_n \int_0^\pi e^{y \cos \theta} \cos(z \sin \theta) \cos n\theta \cos^r \theta d\theta = \pi \partial^r R_n / \partial y^r, \quad . \quad . \quad . \quad (26.1)$$

$$2 \int_0^\pi e^{y \cos \theta} \sin(z \sin \theta) \sin n\theta \cos^r \theta d\theta = \pi \partial^r S_n / \partial y^r, \quad . \quad . \quad . \quad (27.1)$$

$$\epsilon_n \int_0^\pi e^{y \cos \theta} \cos(z \sin \theta) \cos n\theta \sin^{2r} \theta d\theta = (-1)^r \pi \partial^{2r} R_n / \partial z^{2r}, \quad . \quad . \quad (26.2)$$

$$2 \int_0^\pi e^{y \cos \theta} \sin(z \sin \theta) \sin n\theta \sin^{2r} \theta d\theta = (-1)^r \pi \partial^{2r} S_n' / \partial z^{2r}, \quad . \quad . \quad (27.2)$$

$$\epsilon_n \int_0^\pi e^{y \cos \theta} \sin(z \sin \theta) \cos n\theta \sin^{2r-1} \theta d\theta = (-1)^r \pi \partial^{2r-1} R_n / \partial z^{2r-1}, \quad (26.3)$$

$$2 \int_0^\pi e^{y \cos \theta} \cos(z \sin \theta) \sin n\theta \sin^{2r-1} \theta d\theta = -(-1)^r \pi \partial^{2r-1} S_n / \partial z^{2r-1}. \quad (27.3)$$

In (26.2), (26.3) take  $y = n = 0$ :

$$\int_0^\pi \cos(z \sin \theta) \sin^{2r} \theta \, d\theta = (-1)^r \pi d^{2r} J_0(z) / dz^{2r}, \quad (28)$$

$$\int_0^\pi \sin(z \sin \theta) \sin^{2r-1} \theta \, d\theta = (-1)^r \pi d^{2r-1} J_0(z) / dz^{2r-1}, \quad (29)$$

the first of which gives Poisson's integral. If in (24), (25) we increase  $\theta$  by  $s\pi/2$  ( $s=1, 2, 3$ ) we get three further sets of integrals in a similar way.

If in (24), (25) we change  $y$  into  $-y$ , add or subtract the new results and the old, and proceed as above, we obtain integrals such as

$$\int_0^\pi \cosh(y \cos \theta) \cos(z \sin \theta) \, d\theta$$

expressed at once in terms of Bessel's coefficients. As before,  $\theta$  may be replaced by  $\theta + s\pi/2$ , giving a new chain of integrals. Omitting all these we pass to the type

$$\int_0^\pi f(y \phi(\theta)) g(z \psi(\theta)) \, d\theta,$$

where each of  $f, \phi, g, \psi$  is any one of  $\sin, \cos$ .

9. In the definitions of  $R_n, S_n$  replace  $y$  by  $iy$  and separate reals and imaginaries,

$$R_{2n}(iy, z) = T_{2n}(y, z), \quad S_{2n+1}(iy, z) = T_{2n+1}(y, z),$$

both of which are real, and

$$S_{2n}(iy, z) = iU_{2n}(y, z), \quad R_{2n+1}(iy, z) = iU_{2n+1}(y, z),$$

both of which are pure imaginary, where the functions  $T_n, U_n$  are defined by

$$T_n(y, z) \equiv T_n \equiv \epsilon_n J_n(\sqrt{z^2 + y^2}) \left[ \frac{(z + iy)^n + (z - iy)^n}{2(\sqrt{z^2 + y^2})^n} \right],$$

$$U_n(y, z) \equiv U_n \equiv \epsilon_n J_n(\sqrt{z^2 + y^2}) \left[ \frac{(z + iy)^n - (z - iy)^n}{2i(\sqrt{z^2 + y^2})^n} \right].$$

Hence, replacing  $y$  by  $iy$  in (24) we get

$$\cos(y \cos \theta) \cos(z \sin \theta) = \sum T_{2n} \cos 2n\theta, \quad (30)$$

$$\sin(y \cos \theta) \cos(z \sin \theta) = \sum U_{2n+1} \cos(2n+1)\theta, \quad (31)$$

and similarly from (25),

$$\cos(y \cos \theta) \sin(z \sin \theta) = \sum T_{2n+1} \sin(2n+1)\theta, \quad (32)$$

$$\sin(y \cos \theta) \sin(z \sin \theta) = \sum U_{2n} \sin 2n\theta. \quad (33)$$

We shall omit the complete set of similar expansions obtainable by successive increases of  $\theta$  by  $\pi/2$ . The following generalizations of two results due to Jacobi are of interest. By additions and subtractions of (30)–(33) we have

$$\cos(y \cos \theta \pm z \sin \theta) = \sum (T_{2n} \cos 2n\theta \mp U_{2n} \sin 2n\theta), \quad (34)$$

$$\sin(y \cos \theta \pm z \sin \theta) = \sum [U_{2n+1} \cos (2n+1)\theta \pm T_{2n+1} \sin (2n+1)\theta], \quad (35)$$

which for  $y$  or  $z=0$  become the results in question, as also do (30), (31) for  $z=0$ , and (32)  $y=0$ . If in the definitions of  $T_n$ ,  $U_n$  we put  $z=w \cos \phi$ ,  $y=w \sin \phi$ , we get from (30)–(33):

$$\begin{aligned} \cos(w \sin \phi \cos \theta) \cos(w \cos \phi \sin \theta) \\ = \sum \epsilon_{2n} J_{2n}(w) \cos 2n\phi \cos 2n\theta, \quad \dots \quad (36) \end{aligned}$$

$$\begin{aligned} \sin(w \sin \phi \cos \theta) \cos(w \cos \phi \sin \theta) \\ = \sum J_{2n+1}(w) \sin (2n+1)\phi \cos (2n+1)\theta, \quad (37) \end{aligned}$$

$$\begin{aligned} \cos(w \sin \phi \cos \theta) \sin(w \cos \phi \sin \theta) \\ = \sum J_{2n+1}(w) \cos (2n+1)\phi \sin (2n+1)\theta, \quad (38) \end{aligned}$$

$$\begin{aligned} \sin(w \sin \phi \cos \theta) \sin(w \cos \phi \sin \theta) \\ = \sum \epsilon_{2n} J_{2n}(w) \sin 2n\phi \sin 2n\theta, \quad \dots \quad (39) \end{aligned}$$

which, however, can be obtained from the corresponding modifications of (34), (35) by additions and subtractions, and these in turn follow at once from Jacobi's expansions by putting therein  $\phi \pm \theta$  for  $\theta$ . Multiply (30) throughout by  $\cos 2n\theta$  and integrate from 0 to  $\pi$ ,

$$\epsilon_{2n} \int_0^\pi \cos(y \cos \theta) \cos(z \sin \theta) \cos 2n\theta d\theta = \pi T_{2n}, \quad (40)$$

and similarly from (31)

$$2 \int_0^\pi \sin(y \cos \theta) \cos(z \sin \theta) \cos (2n+1)\theta d\theta = \pi U_{2n+1}, \quad (41)$$

while from (32), (33) we get

$$2 \int_0^\pi \cos(y \cos \theta) \sin(z \sin \theta) \sin (2n+1)\theta d\theta = \pi T_{2n+1}, \quad (42)$$

$$2 \int_0^\pi \sin(y \cos \theta) \sin(z \sin \theta) \sin 2n\theta d\theta = \pi U_{2n}. \quad \dots \quad (43)$$

From (36)–(39) we have several double integrals for  $J_n(z)$ , of which the following is one:

$$e_{2n} \int_0^\pi \int_0^\pi \cos(w \sin \phi \sin \theta) \cos(w \cos \phi \sin \theta) \cos 2n\theta \\ \cos 2n\phi d\theta d\phi = \pi^2 J_{2n}(w). \quad (44)$$

As before, by differentiations and changes of the argument, the integrals already indicated furnish many more. If we multiply together the Fourier series for  $\cos(y \cos \theta)$ ,  $\cos(z \sin \theta)$ , which can be written down from (32) by putting  $z=0$ ,  $y=0$  in turn, and equate the coefficient of  $\cos 2n\theta$  to  $T_{2n}$ , we arrive at the expression of  $J_n(\sqrt{z^2 + y^2})$  in terms of Bessel coefficients having the respective arguments  $z$ ,  $y$ . Many other such theorems are sufficiently suggested by the expansions. Thus, the functions of  $y$ ,  $z$  and the identities between them obtained by equating coefficients of like powers of  $\sin \theta$  or  $\cos \theta$  in (30) and other expansions of the same type, are of interest. These are the analogues of the expansions of powers of a single variable in a series of Bessel coefficients.

Finally, a great number of summations involving Bessel coefficients can be effected by multiplying any of the expansions such as (24), (25), (30)–(39) by a power of  $\sin x$  or of  $\cos x$  and integrating between the limits 0,  $\pi$ .

### XXIII. The X-Ray Spectra of the Lower Elements.

By ROBERT THORÆUS\*.

[Plate IV.]

#### PART I.

IN two previous papers†, Prof. M. Siegbahn and the author have given the preliminary results of some attempts to extend the range of registered wave-lengths within the K- and L-Series. This work was found to be attended by many difficulties, among which especially may be mentioned the absorption of this weak radiation. These difficulties,

\* Communicated by Prof. Manne Siegbahn. An abstract of this paper, entitled "Extension of the Range of X-Ray Spectra against Longer Wave-lengths," and containing the wave-lengths and a short description of the high-vacuum spectrograph, was read before a meeting of Danish, Norwegian, and Swedish physicists at Oslo, August 25th, 1925.

† *Arkiv f. Mat., Astr. och Fys.* Bd. xviii. No. 24 (1924); Bd. xix. A. No. 12 (1925).

however, were fairly successfully overcome by building a high-vacuum spectrograph that has been found to be very good for this purpose, and so it has also been used during the present investigation.

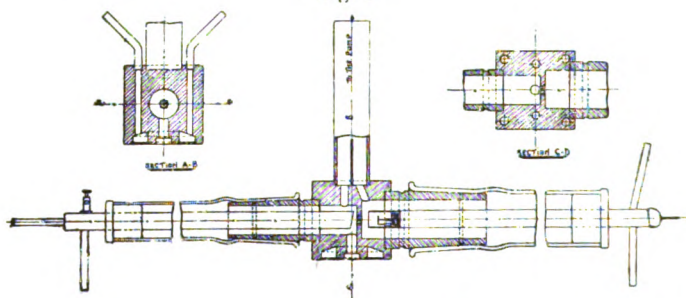
Among the earlier known crystals, gypsum, mica, and sugar are the only ones that can be used for reflecting those long wave-lengths. The upper limit being about  $18 \text{ \AA.U.}$ , they cannot be used for the whole range of wave-lengths investigated here. There are, however, many organic compounds suitable for this purpose. Especially lauric acid and palmitic acid have proved to be good. Their reflecting power is good, and their melting-points so high that they practically do not evaporate in vacuum. In the two papers mentioned above the lattice constant of palmitic acid and some wave-lengths were given. Those values are now checked and together with some new ones given with the best accuracy available within this range of wave-lengths. By other authors it has earlier been pointed out that the X-ray lines become broader and diffuse when the wave-lengths increase. This also appears here. For instance, when taking  $\text{Cu L}\alpha$  by means of gypsum and a slit of  $0.2 \text{ mm.}$  width, I get a line  $2.5 \text{ mm.}$  wide. Because of this it is rather difficult to give very exact values of the long wave-lengths. In order to get the measurements as uniform as possible I have, however, measured all the lines to their maximum of blackening.

The general arrangement of the apparatus has already been published\*. In connexion with this investigation, however, two new types of X-ray tube have been built and tested. When wolfram filaments are used, a thin deposit of metallic wolfram is always to be found on the emission-surface of the anticathode, and in this deposit a strong absorption of the radiation of long wave-lengths will appear. To prevent this absorption a thin metallic foil may be inserted between the cathode and the anticathode. When the electrons pass through this foil their speed will be decreased, but this difficulty can easily be overcome by increasing the tension. Fig. 1 gives the general arrangement of a tube built on this principle. The body of the tube and the cathode and anticathode are of standard make. In the middle of the tube a metallic wall is arranged and fitted with a number of small holes, the diameters of which are about  $1 \text{ mm.}$  By covering the wall on the anticathode side with a thin aluminium foil ( $5\text{--}7\mu$ ) the above deposit is

\* *Arkiv f. Mat., Astr. och Fys.* Bd. xix. A, No. 12 (1925).

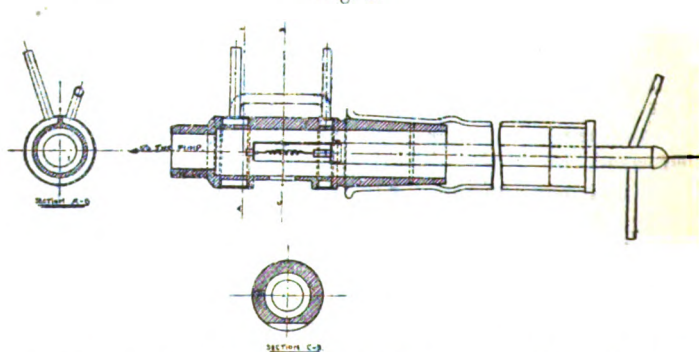
quite eliminated. Moreover, as the window of the X-ray tube is taken away, this arrangement will also protect the photographic plate from fogging by the ordinary light from the hot filament. To get a good cooling of the foil the wall should be rather thick (2–3 mm.), otherwise it would immediately melt because of the heat from the hot filament and the energy that the electrons lose when passing through the foil. The tube itself as well as the cathode and

Fig. 1.



anticathode are supplied with an efficient water-cooling system. Both the cathode and the anticathode are connected to the tube by glass-grindings, thus allowing the tube to be kept working with either one terminal earthed or both of them high-tensioned. For evacuating the tube two channels are arranged, both of them debouching into a wider tube that is connected to the pump. By this arrangement the light from the hot filament cannot come inside the spectrograph and blacken the photographic plate.

Fig. 2.



In fig. 2 the other type of X-ray tube is to be seen. Only the cathode is here standard made. The body of the

tube is cylindrical and supplied with a longitudinal slit the size of which is  $15 \times 2$  mm. The slit is covered by a metallic foil ( $10\mu$ ) soldered to the body of the tube and acting as anticathode, on which the different substances may be placed when their radiation is to be examined. Other details will easily be understood from the drawing.

Both the types have proved to be rather good, especially when working with X-ray spectra of long wave-lengths.

The spectrograms were taken on film strips placed in a circular bent holder and at a distance of 135.70 mm. from the reflecting surface of the crystal.

All the wave-lengths given below are based upon the wave-length of the Na  $K\alpha$  line. Hjalmar\*, in his precision measurements, has found the value Na  $K\alpha \lambda = 11.884$  Å.U. Assuming this value to be right and always working with spectra of the 1st order, the measurements have proceeded in the following way.

The  $L\alpha$  and  $L\beta$  lines of Zn(30) and Cu(29) were determined to Na  $K\alpha$  as reference and by means of a gypsum crystal, the lattice constant of which is

$$d = 7.578 \text{ Å.U. and } \log 2d = 1.8056.$$

From the plates T. 179 and 181 were calculated

$$\text{Zn} \begin{cases} L\alpha = 12.224 \text{ Å.U.} \\ L\beta = 11.958 \text{ Å.U.} \end{cases} \quad \text{and} \quad \text{Cu} \begin{cases} L\alpha = 13.308 \text{ Å.U.} \\ L\beta = 13.029 \text{ Å.U.} \end{cases}$$

Then the  $L\alpha$  and  $L\beta$  lines of Ni(28) and Co(27) were determined to Zn  $L\alpha$  as reference and by using a mica crystal, the lattice constant of which is

$$d = 9.927 \text{ Å.U. and } \log 2d = 1.29786.$$

This value belongs to reflexion in the 1st order, and is taken from an investigation in this laboratory by Mr. Axel Larsson†. From the plates T. 183 and 184 were calculated

$$\text{Ni} \begin{cases} L\alpha = 14.528 \text{ Å.U.} \\ L\beta = 14.235 \text{ Å.U.} \end{cases} \quad \text{and} \quad \text{Co} \begin{cases} L\alpha = 15.940 \text{ Å.U.} \\ L\beta = 15.62 \text{ Å.U.} \end{cases}$$

In order to get the lattice constants of lauric acid and palmitic acid, the  $L\alpha$  lines of Zn(30), Cu(29), Ni(28), and Co(27) were taken as symmetrical double registerings. The following Tables I. and II. give the calculated angles.

\* Phil. Mag. vol. xli. April 1921.

† *Arkiv f. Mat., Astr. och Fys.* Bd. xix. A, No. 14 (1925).



TABLE I.  
Lauric acid.

Plate No.	Line.	Distance mm.	Angle $\phi$ .
186.....	Zn $L\alpha$	89.3	$12^{\circ} 56' 9''$
187.....	Cu $L\alpha$	97.4	$14^{\circ} 7' 4''$
188.....	Ni $L\alpha$	106.6	$15^{\circ} 27' 4''$
189.....	Co $L\alpha$	117.2	$16^{\circ} 59' 6''$

*Note.*—The measured distances in this table refer to 98.6 mm. distance between the crystal and the plate-holder.

TABLE II.  
Palmitic acid.

Plate No.	Line.	Distance mm.	Angle $\phi$ .
198.....	Zn $L\alpha$	94.0	$9^{\circ} 55' 0''$
193.....	Cu $L\alpha$	102.3	$10^{\circ} 47' 6''$
194.....	Ni $L\alpha$	112.0	$11^{\circ} 49' 0''$
195.....	Co $L\alpha$	123.2	$12^{\circ} 59' 9''$

Inserting these angles and the above given wave-lengths corresponding to them in the Bragg formula, we get the following values of the lattice constants:—

*Lauric acid :*

From Zn  $L\alpha$  :  $\log 2d = 1.73683$

Cu  $L\alpha$  :  $\log 2d = 1.73670$

Ni  $L\alpha$  :  $\log 2d = 1.73650$

Co  $L\alpha$  :  $\log 2d = 1.73672$

Mean value :  $\log 2d = 1.73669$  and  $2d = 54.536 \text{ \AA.U.}$

*Palmitic acid :*

From Zn  $L\alpha$  :  $\log 2d = 1.85113$

Cu  $L\alpha$  :  $\log 2d = 1.85167$

Ni  $L\alpha$  :  $\log 2d = 1.85098$

Co  $L\alpha$  :  $\log 2d = 1.85084$

Mean value :  $\log 2d = 1.85116$  and  $2d = 70.98 \text{ \AA.U.}$

Then the  $L\alpha$  and  $L\beta$  lines of Fe (26) and the  $K\alpha$  line of F (9) were taken as symmetrical double registrations by means of palmitic acid, and the plates calculated with the above value of the lattice constant. From the plates T. 196 and 197 the following values are obtained :—

$$\begin{aligned} \text{Fe} \left\{ \begin{array}{l} L\alpha: d=135.9 \text{ mm.}, \quad \phi=14^\circ 20'2, \quad \lambda=17.58 \text{ \AA.U.} \\ L\beta: d=133.1 \text{ mm.}, \quad \phi=14^\circ 2'5, \quad \lambda=17.22 \text{ \AA.U.} \end{array} \right. \\ \text{F} \quad K\alpha: d=141.3 \text{ mm.}, \quad \phi=14^\circ 56'4, \quad \lambda=18.30 \text{ \AA.U.} \end{aligned}$$

Using the palmitic acid as crystal, the L-Series of Mn (25) and Cr (24) were taken to Cu  $L\alpha$  as reference. The plates T. 202 and 215 belong to these exposures and give the following results :—

$$\begin{aligned} \text{Mn} \left\{ \begin{array}{l} L\alpha: \phi=15^\circ 51'4, \quad \lambda=19.39 \text{ \AA.U.} \\ L\beta: \phi=15^\circ 33'7, \quad \lambda=19.04 \text{ \AA.U.} \end{array} \right. \\ \text{Cr} \left\{ \begin{array}{l} L\alpha: \phi=17^\circ 39'1, \quad \lambda=21.53 \text{ \AA.U.} \\ L\beta: \phi=17^\circ 22'0, \quad \lambda=21.19 \text{ \AA.U.} \end{array} \right. \end{aligned}$$

Within the L-Series it has also been possible to measure the weaker doublet  $l\eta$ . For taking this doublet palmitic acid has been used for the elements below 31, and gypsum or mica for those ones above 32. From the following Table III. are to be seen the substances applied to the anticathode, and in Table IV. all the wave-lengths are collected.

TABLE III.

Element No.	Substance applied.	Way of application.
35 Br .....	NaBr (powder).	The copper anticathode was scratched with a knife and the powder pressed into the scratches.
34 Se .....	Se (powder).	
33 As .....	As (powder).	
30 Zn .....	Metallic plate.	
29 Cu .....	Pure anticathode.	The metallic plates were dove-tailed into the emitting surface of the anticathode.
28 Ni .....	Metallic plate.	
27 Co .....	" "	
26 Fe .....	" "	
25 Mn .....	Electrolytic deposit on copper plates.	As the above powders.
24 Cr .....		
9 F .....	NaF (powder).	

TABLE IV. a

Element No.	L $\eta$ .			L $\alpha_1 \alpha_2$ .			L $\beta_1$ .		
	$\lambda$ Å.U.	$\nu/R$ .	$\sqrt{\nu/R}$ .	$\lambda$ Å.U.	$\nu/R$ .	$\sqrt{\nu/R}$ .	$\lambda$ Å.U.	$\nu/R$ .	$\sqrt{\nu/R}$ .
37 Rb .....	—	—	—	8.029 <sup>1</sup>	113.50	10.453	7.303 <sup>1</sup>	124.79	11.171
35 Br .....	9.563	95.29	9.762	9.234	98.68	9.934	8.357 <sup>1</sup>	109.05	10.442
34 Se .....	10.271	84.72	9.419	9.939	91.60	9.576	8.971 <sup>1</sup>	101.58	10.079
33 As .....	11.047	82.50	9.083	10.710	85.08	9.224	9.650 <sup>1</sup>	94.43	9.718
30 Zn .....	13.85	65.33	8.082	13.61	66.96	8.183	12.224	74.55	8.634
29 Cu .....	15.19	59.99	7.746	14.83	61.45	7.839	13.308	68.48	8.275
28 Ni .....	16.55	55.06	7.421	16.17	56.36	7.507	14.528	62.72	7.920
27 Co .....	18.20	50.07	7.076	17.77	51.28	7.161	15.94	57.17	7.561
26 Fe .....	20.12	45.29	6.730	19.65	46.38	6.810	17.58	51.84	7.200
25 Mn .....	—	—	—	—	—	—	19.39	46.98	6.855
24 Cr .....	—	—	—	—	—	—	21.53	42.33	6.506

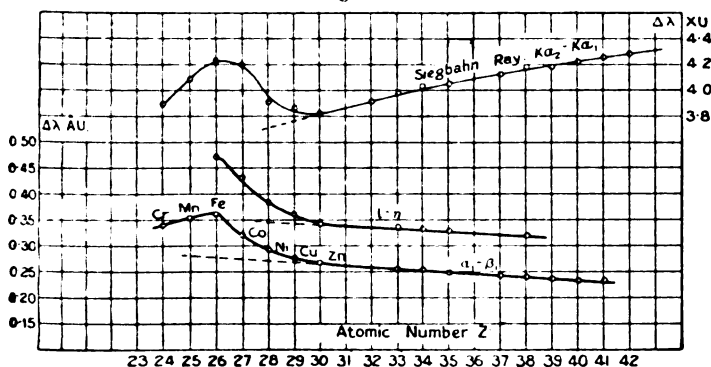
<sup>1</sup> Earlier measurements by other authors.

TABLE IV. b

Element No.	K $\alpha_1 \alpha_2$ .		
	$\lambda$ Å.U.	$\nu/R$ .	$\sqrt{\nu/R}$ .
9 F .....	18.30	49.80	7.057

By calculating the wave-length differences  $L\alpha_1 - L\beta_1$  and  $L\eta - L\eta$ , and plotting them against the atomic number  $Z$  we get the diagram in fig. 3. It is clearly to be seen, how the running of the curves suddenly changes at Cu, and how the values of the elements below Cu form something like a peak the top of which belongs to Fe (26). In an earlier paper Prof. M. Siegbahn and Mr. B. B. Ray\* have studied the doublet-difference  $K\alpha_1 - K\alpha_2$  within this range of elements, and found within the K-Series an effect of the

Fig. 8.



same appearance as the one in fig. 3. This is not a mere chance, but will be quite understood when looking at the energy-level diagram in fig. 4. As may be seen, all the lines  $K\alpha_1$ ,  $K\alpha_2$ ,  $L\alpha_1$ ,  $L\beta_1$ ,  $L\eta$ , and  $L\eta$  are formed by transitions, either from the levels  $L_{II}$  and  $L_{III}$  or to those ones. The small difference between the lines  $L\alpha_1$  and  $L\alpha_2$  is not taken into account, as the dispersion used here is not sufficient to separate them. In consequence of this it may be expected that for every element within this range the differences in  $\nu/R$  of  $(L\beta_1 - L\alpha_2)$ ,  $(L\eta - L\eta)$ , and  $(K\alpha_1 - K\alpha_2)$  should be all the same. How far this is the case will be seen from the following Table V.

The differences  $K\alpha_1 - K\alpha_2$  are calculated from the values in Siegbahn's book, 'The Spectroscopy of X-Rays.'

\* *Arkiv f. Mat., Astr. och Fys.* Bd. xviii. No. 19 (1924).



In Plate IV. I have collected some photograms taken with palmitic acid during this investigation. The film-strips are arranged one above the other with their direct beam blackenings on a vertical.

Upsala, Physical Laboratory of the University.  
September 29th, 1925.

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XXIV. *On the Optical Properties of Chromatic Emulsions.*  
By C. M. SOGANI, M.Sc., Assistant Professor of Physics,  
Benares Hindu University\*.

[Plate V.]

1. *Introduction.*

IT has long been known that emulsions exhibiting structural colour may be obtained by shaking up glycerine and turpentine, the phenomenon arising from the fact that the liquids have equal refractive indices for some particular part of the spectrum but not for others. These emulsions are, however, somewhat transient as the liquids speedily separate into distinct layers. Recently, Holmes and Cameron† have succeeded in preparing a considerable variety of coloured emulsions using a suitable emulsifying agent and choosing for the continuous phase a mixture whose refractive index may be continuously adjusted by varying its composition. The emulsions obtained in this way are fairly permanent and are exceedingly beautiful by reason of the play of colours which they exhibit. Qualitative studies of the optical effects exhibited by glycerine-turpentine emulsions were carried out some years ago at the suggestion of Prof. C. V. Raman by N. K. Sethi‡. The present work was also undertaken at his instance to study the optical properties of the emulsions obtained with an emulsifying agent, the comparative permanence of which greatly facilitates the work and widens the range of investigation. The research undertaken included a study of the spectral range of the light transmitted by the emulsions, their refractivity, the character of the diffraction-haloes produced by them, their surface colours, and the influence of the dispersive powers of the liquid used, of the particle-size,

\* Communicated by Prof. C. V. Raman, M.A., D.Sc., F.R.S.

† Am. Chem. Soc. Journ. xlv. pp. 71-74, Jan. 1922.

‡ N. K. Sethi, Proceedings of the Indian Assn. for the Cult. of Science, vol. vi. p. 134 (1920-21).

and of the depth of the emulsion on its optical behaviour. The paper sets out the results of work carried out on these points, together with a theoretical discussion. Probably the most interesting new phenomenon noticed in the course of the experiments is that the light scattered by an emulsion in which the disperse phase consists of droplets of uniform size closely packed together is concentrated in sharply-defined circular diffraction-rings, the effect being somewhat analogous to that obtained with monochromatic X-rays in the powder method of crystal analysis.

## 2. *Some Observations with Non-homogeneous Emulsions.*

We shall deal in this and the two following sections with emulsions containing particles of non-uniform size. The case of uniform particles will be considered later in the paper.

For the observations described below, some of the emulsions mentioned by Holmes and Cameron were prepared and used.

*Spectrum of the Transmitted Light.*—To determine the spectrum of the transmitted light, the image of a small source of white light was formed by means of a lens on the slit of a wave-length spectrometer placed 2 or 3 metres away from the source. The cell containing the emulsion was placed just in front of the lens (between it and the source). The spectral region of transmission obtained is always quite narrow. It is not, however, an invariable quantity, but is found to be dependent on a number of factors. To give an idea of the range of transmission, a particular case of the emulsion of glycerine in a mixture of benzene and acetone may be mentioned here. In this case, with a thickness of the emulsion of 3 cm. and a mean diameter of the particles of  $\cdot 003$  cm., the region of transmission amounts to about  $200 \text{ \AA U.}$  in the yellow, the particles being closely packed together.

*Effect of the Intensity.*—The region of transmission is found to widen as the intensity of the incident beam is increased and *vice versa*. If the experiment be performed with sunlight in a somewhat cloudy weather, the width of the spectrum is found to diminish remarkably as an occasional cloud passes across the sun. This observation clearly indicates that the spectral energy-curve of the transmitted light is not sharply bounded on either side of the wave-length of maximum transmission, but falls off very rapidly at first and later more slowly. The variation of transparency with wave-length could well be represented by

a graph of the same form as the well-known probability curve.

*Effect of Thickness.*—The region of transmission decreases as the thickness of the emulsion increases and *vice versa*, nearly the complete spectrum being transmitted through a thickness of the order of .1 mm. The effect of varying thickness can be studied in a simple and interesting way by placing a hollow prism containing the emulsion on the table of a spectroscope, the aperture of the pencil of light passing through it being restricted by interposing a slit cut in an opaque card. As the slit is moved along the face of the prism away from its edge, the narrowing of the visible region of the spectrum is conspicuous.

*Effect of Particle-size.*—Emulsions in which the particles of the disperse phase are finer transmit a wider region than those containing coarser particles. The average size of the particles can be varied by adjusting the vigour and period of shaking of the emulsion either with the hand or with a mechanical emulsifier. Actually, the region of transmission was found to widen about 5 times when the average particle-size was reduced from 1 mm. to .05 mm.

*Effect of Concentration of the Disperse Phase.*—The width of the transmitted spectrum alters with the concentration of the disperse phase. A very dilute emulsion transmits nearly the complete spectrum. As the concentration is increased, the spectrum becomes narrower, approaching a limit in the case of close packing.

*Effect of the Relative Dispersive Powers.*—All other conditions remaining the same, emulsions in which the dispersive powers of the two phases are more widely different transmit a narrower region of the spectrum. For example, this region is about half as wide in the case of an emulsion of glycerine in a mixture of carbon disulphide and acetone as in the case where glycerine is dispersed in a mixture of benzene and acetone. It need hardly be mentioned that the so-called transparent emulsions in which the two phases have nearly the same dispersive power transmit the complete spectrum.

*Light-scattering by the Emulsion.*—When a point source of white light is observed through the emulsion, a continuous halo exhibiting a finely-mottled structure in which the colour changes from place to place appears to surround the source which, of course, has the colour of the transmitted light, the sequence of colours in the halo depending on the region of transmission. If monochromatic light be used, the size of the halo is found to be a minimum for the wave-length



for which the two phases have the same refractive index and increases on either side of this region. Further, the size of the halo (1) increases with the intensity of the incident beam, showing that the distribution of intensity about the centre must be here also of the error-law type; (2) increases with the thickness of the emulsion; (3) decreases with an increase in the size of the particles; and (4) increases with the concentration of the disperse phase.

The spectrum of the light scattered in directions variously inclined to that of incidence may be observed by focussing it on the slit of the spectroscope. When the direction of scattering differed a little from that of incidence, the spectrum observed was quite narrow, possessing a narrow dark line in the middle corresponding to the middle of the region of transmission. At greater obliquities, both the bright and dark parts of the spectrum widened considerably.

### 3. *Theory of Light Propagation in Non-Homogeneous Emulsions.*

An explanation of the observed variations of transparency of the emulsions may be attempted on the principles of the wave-theory in the following way.

Let us suppose a plane wave to be incident on a cell containing the emulsion. As it passes through, any specified element of its area would encounter the particles of the disperse phase, and would thereby be retarded to an extent depending on the number of such encounters, the size of the particles, and the difference of refractive indices. On account of the random distribution of size amongst the particles, the number of encounters and therefore the retardation corresponding to the different portions of the wave-front will be different. The total area of the portions of the wave-front corresponding to the range of encounters lying between  $m+x$  and  $m+x+dx$  may be assumed to be proportional to  $\exp. - \left(\frac{x^2}{2m}\right) dx$ ,  $m$  being the most probable number of encounters. If the average path through the disperse phase for a single encounter be  $p$ , the average vibration due to a unit area of the complete wave-front will be

$$y = \frac{\int_{-\infty}^{+\infty} \exp. - \left(\frac{x^2}{2m}\right) \cos \left\{ wt - \frac{2\pi}{\lambda} (\mu - \mu') . xp \right\} dx}{\int_{-\infty}^{+\infty} \exp. - \left(\frac{x^2}{2m}\right) dx} .$$

where  $\mu$  and  $\mu'$  are the refractive indices of the two phases for wave-length  $\lambda$ .

This gives for the average intensity

$$T = \exp. - \left[ 4\pi^2 m \left( \frac{\mu - \mu'}{\lambda} \right)^2 p^2 \right]. \quad . \quad . \quad . \quad (1)$$

If we assume a close packing,  $m$  would be approximately equal to the thickness  $t$  of the emulsion considered divided by  $d$ , the average diameter of a particle. To determine  $p$ , we have first to take the average of the paths corresponding to the various elements of the surface of a particular droplet, and then again take the average for the various sizes of the particles. This can be easily seen to be  $p = \frac{2d}{3}$ , where

$d$  is the average diameter of a particle.

Substituting for  $m$  and  $p$  in (1) we get

$$T = \exp. - \left[ \frac{16}{9} \pi^2 \left( \frac{\mu - \mu'}{\lambda} \right)^2 t d \right] \quad . \quad . \quad . \quad (2)$$

To test equation (2) the following arrangement of apparatus was employed. The light from a strong source a few millimetres square in area passed through the cell containing the emulsion, the aperture of the pencil being restricted to about 1 cm., and formed an image of the source on a distant screen containing a small hole  $\frac{1}{2}$  mm. diameter. The light passing through fell upon one of the windows of a Hilger-Nutting spectrophotometer, placed at a distance of about 30 cm. behind the last screen. The size of the apertures used and their distance apart are matters of great importance in order to ensure that in the light entering the spectrometer the scattered light is excluded as completely as possible. The other window of the spectrophotometer was illuminated directly by the original source, the intensity being cut down to a suitable value by an absorbing screen. The emulsion studied was one of glycerine in a mixture of acetone and benzene, and was made up of measured volumes of the liquids so chosen that glycerine comprised about 74 per cent. of the whole. Some of the results obtained are appended in the following table.

$$t = 3 \text{ cms. ; } d = .0027 \text{ cm.}$$

$\lambda \text{ cms.}$ $\times 10^{-5}$	$\exp. - \left[ \frac{16}{9} \mu^2 d \left( \frac{\mu - \mu'}{\lambda} \right)^2 \right]$	$\exp. - \left[ 9td \left( \frac{\mu - \mu'}{\lambda} \right)^2 \right]$	Observed Intensity.
6100	.0025	.08	.10
6080	.004	.22	.24
6040	.30	.61	.65
6020	.61	.82	.84
6000	.94	.98	.98
5980	.94	.98	.98
5960	.62	.83	.82
5940	.30	.62	.74
5920	.09	.37	.49
5900	.004	.22	.31
5880	.0025	.08	.13

In the above table, the second column contains the values as calculated from the formula derived above, and the fourth the values observed photometrically. The constant used for calculation in col. (3) is 9 instead of  $\frac{16}{9} \pi^2$ . On account

of the vast reduction in the quantity of light due to the several small apertures, the photometric observations could not be carried out very accurately. The values in col. (3) agree much better with the observed values than those in col. (2). This discrepancy is probably due to scattered light still getting into the apparatus, which fact will certainly increase the values of observed intensities at every part of the transmitted spectrum, the difference being more marked towards the two ends, as there the real intensity due to the transmitted light itself would be very small.

*Refractivity of the Emulsion.*—If a wave of light be incident on the emulsion, its path will lie partly through the disperse phase and partly through the continuous medium. The emulsion as a whole will therefore have a definite refractive index and dispersive power of its own as distinct from those of either phase and of course intermediate between them. Following up the considerations set forth above, we can find expressions for the refractive index and dispersive power of the emulsion in terms of the corresponding quantities for the two phases. The total average path through the disperse phase will be the product of the average or most probable number  $m$  of encounters

and the average path  $p$  for a single encounter. This will give  $\frac{2t}{3}$  for the total average path through the disperse phase, the remainder of the path  $\frac{t}{3}$  lying through the continuous medium. If  $\mu$  and  $\mu'$  are the refractive indices of the disperse and continuous phases respectively, the refractive index  $\mu_e$  of the emulsion will be

$$\mu_e = \frac{2\mu}{3} + \frac{\mu'}{3}.$$

The dispersive power of the emulsion will also be given by a similar expression,

$$d_e = \frac{2d}{3} + \frac{d'}{3}.$$

These relations were tested in the following way, using the emulsion of glycerine in a mixture of acetone and benzene. The angular dispersions between the two extreme bright green lines of the copper arc were measured with a spectrometer for the glycerine, the mixture of acetone and benzene, and the emulsion, putting them successively in the same hollow prism. The transmission through the emulsion was adjusted in the green. As the region of transmission is very narrow, two wave-lengths farther apart could not be used and the dispersions could not be greater. The results of the observations made are given below :—

Mean $d$ .		Mean $d'$ .		$\frac{2d}{3} + \frac{d'}{3}$ .		Observed mean $d_e$ .	
min.	sec.	min.	sec.	min.	sec.	min.	sec.
3	10	6	30	4	17	4	50

#### 4. *Theoretical Discussion of Light-scattering by Emulsions.*

Since the droplets in the emulsions are considerably larger than the wave-length of light, the distribution of the scattered light in the halo may be determined by considerations of geometrical optics only. For simplicity, we shall consider only the deviations by refraction occurring when a ray passes through a droplet, ignoring internal and external reflexions, etc.\*

\* For a detailed study of the optical effects occurring when light passes through a droplet suspended in a medium of nearly equal refractive index, see N. K. Sethi, *Phil. Mag.* xlii. p. 669.

The deviation of a ray consequent upon successive encounters with a large number of particles of the disperse phase would be determined by the laws of probability; the problem is mathematically the same as the well-known case of the random walk\*. If  $\alpha$  be the average deviation of a ray at a single encounter, the probability that after  $n$  encounters the angle between the original and final directions of the ray will lie between  $\theta$  and  $\theta + d\theta$  will be given by

$$\frac{2}{n\alpha^2} \cdot \exp. - \left[ \frac{\theta^2}{n\alpha^2} \right] \cdot \theta d\theta.$$

The area on a screen receiving the scattered rays between directions  $\theta$  and  $\theta + d\theta$  will, however, be proportional to  $\theta d\theta$  for small values of  $\theta$ . The intensity of the scattered light in direction  $\theta$  will then be given by

$$I = \text{const.} \exp. - \left( \frac{\theta^2}{n\alpha^2} \right).$$

In the case of a closely packed emulsion,  $n = \frac{t}{d}$ . To determine  $\alpha$ , we have first to find the value of the deviation for a given angle of incidence  $i$ , and then take the average in the manner employed for evaluation of  $p$  in equation (1). If we remember that the deviation  $d\theta$  at a single encounter is small, we have directly from Snell's law

$$de = \frac{2(\mu - \mu')}{\mu} \tan i,$$

the number 2 corresponding to the two refractions occurring at each encounter. The average value  $\alpha$  taken over the various angles of incidence can then be seen to be  $\pi \left( \frac{\mu - \mu'}{\mu} \right)$ .

Substituting these values of  $n$  and  $\alpha$ , we have

$$I = \exp. - \left[ \frac{d\mu^2}{\pi^2 t (\mu - \mu')^2} \cdot \theta^2 \right] \times \text{const.} \quad \dots (3)$$

To test (3), a general value B for the numerical constant was assumed in place of  $\frac{1}{\pi^2}$ . B was then determined in the following way. A narrow beam of monochromatic light (the green of the mercury arc) was allowed to fall on the cell containing the emulsion, the refractive indices of the

two phases being made equal for the yellow lines. A screen was placed at a distance of a few cms. from the cell. The size of the halo on the screen depends upon the intensity of the beam employed. By using two small circular apertures of different diameters  $l_1$  and  $l_2$  in the path of the light, beams of intensities proportional to  $l_1^2$  and  $l_2^2$  were obtained and the angles  $\theta_1$  and  $\theta_2$  corresponding to the boundary of the halo in the two cases were measured. Assuming that the intensity at the boundary corresponds to a certain minimum perceptible value for a given wave-length,

$$l_1^2 \cdot \exp. - \left[ \frac{Bd\mu^2}{t(\mu - \mu')^2} \theta_1^2 \right] = l_2^2 \cdot \exp. - \left[ \frac{Bd\mu^2}{t(\mu - \mu')^2} \theta_2^2 \right],$$

from which  $B$  can be easily calculated.

The values of  $B$  as measured were  $\cdot 08$  and  $\cdot 13$ , which are in fair agreement with the theoretical value  $\frac{1}{\pi^2}$ .

### 5. Homogeneous Emulsions.

The homogenization was effected by the process of sedimentation. It is well known, according to Stokes' law, that the constant velocity with which a particle falls in a liquid is greater the bigger the particle. If, then, we have a long column of rather thin freshly shaken non-homogeneous emulsion, a natural and at least partial homogenization of the emulsion will occur as the result of sedimentation, the particles being arranged in different layers more or less according to their size, the coarser particles mostly going into the lower layers and the finer remaining in the upper ones. The homogenization will, of course, be complete only in the topmost layers. Pl. V. figs. 1 and 2 are microphotographs of the sedimented emulsion taken at two different depths. The total length of the column was about 15 cm., and the length occupied by the emulsion after complete sedimentation 5 cm. The two figures correspond respectively to distances about  $\cdot 3$  and 2 cm. below the top. As the contrast obtained in the ordinary chromatic emulsion is too delicate to be successfully photographed, an opaque emulsion of glycerine in acetone was employed for the purpose. A drop or two of the emulsion was sucked off with a fine syringe from the desired depth. Fig. 3 is a photograph of the non-homogeneous emulsion.

So far as the transmitted light is concerned, these emulsions exhibit properties somewhat similar to those of the non-homogeneous type. The diffraction halo, however,

exhibits some very remarkable features for some distance below the surface of separation, which we will now proceed to describe. The ordinary continuous halo of the non-homogeneous emulsion gives place in this case to a beautiful system of maxima and minima, the rings increasing remarkably in size as the surface of separation is approached. The region surrounding the source is dark, then follows a fairly sharp bright ring bluish on the inside and reddish on the outside. This first ring is quite easy to observe, but, with a little practice, a second and sometimes a third bright ring also can be clearly seen even with the hand-shaken emulsion. If, however, the shaking be done by means of a mechanical emulsifier, the rings are more distinct and larger and the second ring can be seen very easily. It is, however, interesting to note that even in white light all the colours are not equally prominent in the ring system. As a matter of fact, at first sight the rings appear to have only the colour of the directly transmitted light, the other colours on either side being too faint to be easily distinguishable. If, however, a monochromator is employed for the observations, the ring system can be observed over a large part of the spectrum and the influence of wave-length on the size of the rings as well as on the intensities of their maxima can be conveniently studied. For the wave-length for which  $\mu = \mu'$ , the scattered light is found to vanish altogether. On either side of this point the rings reappear, the intensity of the maxima first increasing and then diminishing again. Far away from the region of direct transmission, the ring system cannot be observed at all. Moreover, the size of the rings increases continuously with increase of wave-length. Strangely, this size is not at all influenced by the thickness of the emulsion. Pl. V. fig. 4 is a photograph of the phenomenon taken with the violet light of the mercury arc. The width of the incident pencil was restricted by the use of a small aperture before the cell containing the emulsion.

To get a good picture, the region of transmission has to be carefully adjusted. The exposure given was 30 minutes. With much longer exposure, the volatile liquids composing the emulsion evaporate partly, and the adjustment is altered. It was for this reason that a denser photograph could not be obtained. Even as it is, the photograph shows the first ring clearly and the second ring is also faintly visible. The bright line across is due to some scratches on the surface of the cell.

*Theory of the Diffraction Rings.*—An explanation of this interesting phenomenon may be attempted in the following

way. As has been mentioned, at a given depth in the homogeneous emulsion the particles are all more or less of the same size. Consequently there is now no randomness in their distribution, and the exponential law (equation 3) no longer holds good for the distribution of intensity in the halo. On the other hand, due to their more regular spacing, the waves scattered from the various particles will be in a position to interfere, giving the observed maxima and minima, the maxima being comparatively sharp on account of the large number of particles taking part, analogous to a large number of lines in a diffraction-grating. The reason why all the colours are not equally represented in the ring system is that the light scattered by any particular row of particles in a given layer has to pass through the whole layer, partly before and partly after diffraction, and only the wave-lengths near about the point  $\mu = \mu'$  have a chance of getting through. This would at first seem to mean that the intensity of the halo should be a maximum for the values of  $\lambda$  in the immediate neighbourhood of  $\mu = \mu'$ ; but if we remember that the total scattered light in this region would be small also, we shall be able to understand why the brightness of the ring system first increases as we pass from the point  $\mu = \mu'$  and then diminishes again.

A mathematical expression for the size of the rings can be easily obtained if we remember that in a closely packed emulsion the distance between the adjacent diffracting centres will be equal to the diameter of the particles. This would give for the angular distance  $\theta_n$  from the centre, in the case of the  $n$ th maximum the relation

$$\sin \theta_n = n\lambda/d. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

To test equation (4),  $\theta_1$  for the first ring was measured by getting its image on the ground-glass screen of a camera focussed for infinity and placed quite close to the emulsion. A narrow beam of intense light was passed through the emulsion at a suitable definite point. A set of observations taken is given below.

$$\lambda = 6 \times 10^{-5} \text{ cm. ; } d = .002 \text{ cm.}$$

From equation (4) :

$$\theta_1 = \sin \theta_1 = .03 \text{ radian.}$$

$$\theta_1 \text{ as observed} = .025 \text{ radian.}$$

The agreement is fairly close, considering the difficulties involved in the accurate measurement of  $d$ .



*Surface-Colours.* Another optical effect exhibited by the emulsion on settling down is the sparkling colour observed at the boundary plane between the settled emulsion below and the clear liquid above. This colour is observable from both the sides of the boundary surface at nearly grazing incidence. It changes in a beautiful way with the direction of observation, and also depends upon the colour of the light transmitted through the emulsion. A spectroscopic study of the light reflected from the two surfaces was made by the writer. For this purpose the surface was illuminated with light coming from a horizontal slit and observed through a direct-vision spectroscope with the slit horizontal. The emulsion used was that of glycerine in a mixture of acetone and benzene. The transmission was adjusted to be in the middle green. In the case of reflexion from the upper surface, the usual spectrum with the exception of a dark band in the green was obtained at moderate obliquities. At greater obliquities, however, there was a remarkable brightening of the spectrum first in the violet, which gradually extended itself towards the dark band in the green. No such brightening was, however, observed on the red side. On the other hand, reflexion from the lower surface showed a similar brightening on the red and none on the violet side. These effects may be explained in the following way. As we have seen in sect. 3, the emulsion as a whole possesses a definite dispersive power different from that of either phase. The refractive index of the settled emulsion below will therefore be different from that of the mixture of acetone and benzene above except, of course, for the transmission region in the green. It will have a lower refractive index towards the violet and higher towards the red, in this particular case, than the upper liquid. Consequently at suitable angles, which will be very near grazing, since the two dispersive powers are only slightly different, the light towards the violet side of the green will be totally reflected from the upper surface and that on the red side from the lower surface. The dark line always present in the green is due to perfect transmission and therefore complete absence of reflexion in that region, on account of the equality of refractive indices there.

#### 6. Summary.

The paper describes the results of a detailed theoretical and experimental study of the optical properties of chromatic emulsions.

### 1. *Non-homogeneous Emulsions.*

(a) The range of wave-lengths transmitted by these emulsions, which is generally narrow, has been found to depend upon the intensity of the incident light, the thickness of the emulsion, the average particle-size, concentration of the disperse phase, and the difference in the dispersive powers of the two phases.

(b) A theoretical treatment, based on the principles of the wave-theory and the theory of probability, has been given as regards the intensity of the transmitted light. The expression obtained is

$$I = \exp. - \left[ \frac{16}{9} \pi^2 t d \left( \frac{\mu - \mu'}{\lambda} \right)^2 \right].$$

(c) It has been shown both theoretically and experimentally that the emulsion as a whole has a definite refractivity of its own related to that of the two phases by a simple formula.

(d) An expression has been obtained for the distribution of intensity in the halo from considerations of geometrical optics and the laws of chance. This has been verified.

### 2. *Homogeneous Emulsions.*

(a) The emulsions containing particles of uniform size are obtained by the process of sedimentation. The light scattered by these emulsions does not give a continuous halo but is concentrated in well-defined circular diffraction-rings, the effect being somewhat similar to that obtained with monochromatic X-rays in the powder method of crystal analysis. The expression  $\sin \theta_n = n\lambda/d$ , obtained for the angular diameter of the first ring, has been verified.

(b) The surface of separation between the sedimented emulsion below and the clear liquid above shows sparkling colours on both the sides. A spectroscopic study shows that they are due to total reflexion, the emission as a whole possessing a different dispersive power from that of the clear liquid above.

In conclusion, the writer has much pleasure in recording his indebtedness to Prof. C. V. Raman for his invaluable guidance throughout the course of the work, which was carried out at the Laboratory of the Indian Association for the Cultivation of Science.

Calcutta,  
July 23rd, 1925.

XXV. *The Pressures developed on Explosion of Gaseous Mixtures at High Densities.* By W. T. DAVID, Sc.D., M.Inst.C.E., Professor of Engineering, University of Leeds\*.

**I**N a recent paper by Bone, Newitt and Townend† it is shown that during the explosion of inflammable gaseous mixtures contained in a closed vessel the ratio of the maximum pressure developed to the initial pressure of the mixture before explosion increases to a marked extent as the initial pressure increases. Thus this ratio for a 28·5 per cent. mixture of hydrogen and air increases from 7·7 when the initial pressure of the mixture is 3 atmospheres to 8·82 when the initial pressure is 150 atmospheres—an increase of 14·3 per cent.; while with mixtures of carbon monoxide and oxygen diluted with argon, nitrogen, oxygen, or carbon monoxide the increase in the ratio when the initial pressure is varied through the same range is practically twice as great.

Professor Bone and his collaborators regard this increase in the ratio with initial pressure as “unexpectedly large,” and they suggest that it may be due to the “increasing opacity of the gaseous medium with pressure to radiation emitted during the explosion.”

If I understand their views correctly, their suggestion is that on account of increasing opacity to radiation with mixture density the gaseous mixtures during the explosion period do not lose so large a proportion of their heat to the cold walls at high densities as at low densities, and consequently in the high density mixtures a larger proportion of the heat of combustion remains at the moment of maximum pressure than in the low density mixtures. My experience of radiation measurements in gaseous explosions leads, however, to the conclusion that this hypothesis could not account for more than a small fraction of the increase in the pressure ratio because, although the rate of heat loss by radiation may be very great during the explosion period, this period is so small in the experiments that the total heat loss cannot be a very appreciable fraction of the heat of combustion of the gaseous mixtures.

There are probably several causes contributing to the

\* Communicated by the Author.

† Proc. Roy. Soc. cviii. p. 393 (1925).

development of higher pressure ratios with increasing density. Among them may be mentioned the following:—

- (i.) The departure of gases from Boyle's law.
- (ii.) The more rapid attainment at the higher densities of equilibrium conditions between the vibratory and rotational and translational energies of the molecules constituting the products of combustion.
- (iii.) A smaller relative heat loss in the denser mixtures during the explosion period.
- (iv.) A smaller proportion of dissociation in the high density mixtures.
- (v.) More complete combustion in the denser mixtures at the moment of maximum pressure.
- (vi.) A decrease in the specific heat of the gaseous products of combustion at the high temperatures developed as the density of the gaseous mixtures increases.

I believe that causes (i.) to (iv.) are relatively unimportant and that the main causes responsible for the increase in the pressure ratio with density are (v.) and (vi.).

In regard to (v.) a study of the explosion and cooling curves taken by Bone, Newitt and Townend at varying initial pressures will, I think, offer convincing proof that combustion is more complete at the moment of maximum pressure as the density increases. An examination of the series  $2\text{CO} + \text{O}_2 + 4\text{Ar}$  and  $2\text{CO} + \text{O}_2 + 4\text{O}_2$  at initial pressures varying from 3 atmospheres to 75 atmospheres\* will be particularly illuminating in this connexion, and indeed Professor Bone and his collaborators agree that their experiments show distinct evidence of "after-burning" (or incomplete combustion at the moment of maximum pressure) at the lower densities†.

But it is in regard to (vi.) that I wish particularly to direct attention in this paper. Some experiments of mine indicate that the specific heat of gases like  $\text{CO}_2$  and steam which emit (infra-red) radiation when heated and which constitute the products of combustion of the exploded mixtures, decreases to a considerable extent as the density increases at temperatures at which they emit radiation strongly; and it seems to me that this is one of the main causes—possibly the main cause—of the increase of the ratio of the maximum

\* Proc. Roy. Soc. A, cv. pp. 418 & 422 (1924).

† Proc. Roy. Soc. A, cviii. p. 402 (1925).

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pressure developed to the initial pressure as the initial pressure increases.

As this is a point of considerable importance it is desirable to describe briefly the experimental basis for the suggestion.

I found that the intrinsic radiance from a layer of gaseous mixture after explosion of thickness inversely proportional to the density decreased at any given temperature as the density increased when the value of the intrinsic radiance was corrected for absorption\*. The following table, which relates to the 15 per cent. mixtures of coal-gas and air after explosion, shows this clearly †.

Mean absolute temperature of gaseous mixture (°C. abs.).	Intrinsic radiance corrected for absorption from:—			
	2 cm. at $\frac{1}{2}$ atmosphere density.	1.33 cm. at $\frac{1}{4}$ atmosphere density.	1 cm. at 1 atmosphere density.	0.8 cm. at $1\frac{1}{4}$ atmosphere density.
2300	0.41	0.42	0.39	0.37
2200	0.38	0.4	0.36	0.32
2000	0.32	0.33	0.27	0.27
1800	0.23	0.21	0.20	0.19

Great accuracy is not claimed for the values of the corrected intrinsic radiance given in this table because (except in one case) they have been calculated from observed measurements of the intrinsic radiance from two thicknesses of the gaseous mixtures only. I think, however, they show definitely that at any given temperature the intrinsic radiance corrected for absorption from thicknesses of the gaseous mixtures inversely proportional to the density decreases to a considerable extent as the density increases—even within the limits of density  $\frac{1}{2}$  atmosphere to  $1\frac{1}{4}$  atmospheres.

Now since all the gaseous mixtures were of the same composition, thicknesses inversely proportional to the density contained the same number of radiating molecules (mainly CO<sub>2</sub> and steam) and since the intrinsic radiance values have

\* The value of the intrinsic radiance corrected for absorption from a layer of gas is that which would have been actually measured had the gas been perfectly transparent.

† This table has been taken from a paper written in 1911 (Phil. Trans. A, cxi. p. 406). Full information relating to the experimental method will be found in that paper.

been corrected for absorption, it will be clear that the figures given in the table are proportional to the radiation emitted per radiating molecule under the conditions indicated in the table. Thus the radiation emitted per radiating molecule when the gaseous mixtures are at any given temperature decreases as the density of the gaseous mixture increases, and therefore at any given temperature the vibratory energy contained by these molecules decreases as the density of the system containing them increases.

Accepting this result it will at once be clear that the specific heat of gases like  $\text{CO}_2$  and steam will decrease as the density increases at temperatures at which they emit infra-red radiation, in other words, at temperatures at which the vibratory degrees of freedom share in the heat motion of the molecules, for the specific heat of a gas is of course dependent upon molecular vibratory energy as well as upon translational and rotational energy.

In previous papers (Phil. Mag. Feb. 1913, p. 267, and May 1920, p. 551) I have attempted to show how these results may be explained in terms of the kinetic theory of gases, and a reference to those papers will show that for any given temperature the molecular vibratory energy, and therefore the specific heat, tend towards a minimum value at very high densities. This is in accord with the experiments of Bone, Newitt and Townend, for they show that the pressure ratio tends towards a constant value at the higher densities employed in their experiments.

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XXVI. *The Electrification of Two Intersecting Planes.* By  
W. B. MORTON, M.A., *Queen's University, Belfast* \*.

*Summary.*

THE first part of this paper is concerned with the two-dimensional problem of planes of infinite length, in the direction of their intersection, but of finite breadth. This is solved by the method of conformal representation devised by Schwarz. The differential equation which expresses the transformation is found to be integrable so that the coordinates of a point in the electric field can be simply expressed in terms of the logarithmic potential and the line of force function.

\* Communicated by the Author.

*Phil. Mag.* S. 7. Vol. 1. No. 2. Feb. 1926.

Z

The following theorems relating to the distribution of the charge are proved :—

- (1) Half of the entire charge is borne on the outer side of one plane together with the inner side of the other ;  
or,  
The excess of the charge on the outer side of a plane over that on the inner side is the same for the two planes.
- (2) When the two planes have equal breadths and are inclined at angle  $(\pi - \gamma)$  the charge on the convex side is to that on the concave side in the ratio of

$$\frac{1}{2}\pi + \sin^{-1}(\gamma/\pi) \quad \text{to} \quad \frac{1}{2}\pi - \sin^{-1}(\gamma/\pi).$$

In particular, when the planes are equal and at right angles the outer charge is double the inner. A drawing is given (fig. 3) of the lines of force and equipotentials for this case and the distribution of charge on two rectangular planes is discussed in detail.

The analysis is, of course, applicable to the corresponding cases of fluid motion. It leads to a solution of the problem of steady flow past the two planes, when no surfaces of discontinuity are formed. This will be discussed in a following paper.

The diagrams in the second part of the paper (figs. 8-13) illustrate the familiar case of two planes of infinite breadth. Although this is discussed in all the text-books, I do not know any in which a range of figures is given, showing the progressive alteration of the field as the inclination is changed. I publish these at the suggestion of a friend in the hope that some other teachers may find them of interest. I have negatives of the drawings which I shall be glad to lend to any who wish to make copies.

The spiral diagram to illustrate the charge distribution is perhaps new.

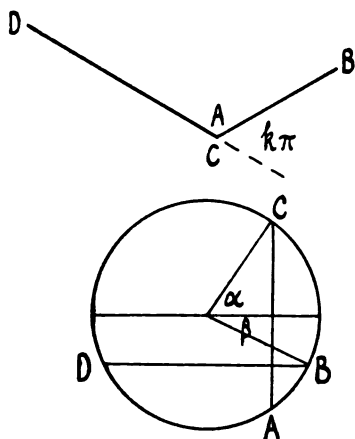
### *Planes of Finite Breadth.*

Let the exterior angle between the planes be  $k\pi$ . The four faces of the two planes are to be regarded as the sides of a collapsed quadrilateral and the surrounding field in the plane of  $z = (x + iy)$  is to be represented on the interior of unit circle in the plane of a second complex variable  $\zeta$  (fig. 1). When this is effected the logarithm of  $\zeta$  gives, in its real and imaginary parts, the potential function and the

function which represents the lines of force in the field surrounding the freely charged planes\*.

If we go round the quadrilateral so as to keep the field

Fig. 1.



on the left the swerves at A, B, C, D are  $k\pi$ ,  $-\pi$ ,  $-k\pi$ ,  $-\pi$ , respectively. Therefore the connexion between

$$z \text{ and } \zeta = \rho e^{i\phi}$$

is given by

$$dz/d\zeta = C\zeta^{-2}(\zeta-a)^{-k}(\zeta-b)(\zeta-c)^k(\zeta-d), \quad (1)$$

where  $a, b, c, d$  are the values of  $\zeta$  at the points on the unit circle corresponding to A B C D in the  $z$ -plane. The choice of these points is limited by the consideration that the expansion of the right-hand side for large values of  $\zeta$  must not contain a term in  $\zeta^{-1}$ , since obviously there cannot be a term in  $\log \zeta$  in the  $(z\zeta)$  relation. So we must have

$$-ka + b + kc - d = 0. \quad (2)$$

If  $\phi_1, \phi_2, \phi_3, \phi_4$  are the arguments of the complex quantities  $a, b, c, d$ , the above equation gives the two relations,

$$\left. \begin{aligned} \cos \phi_2 + \cos \phi_4 &= k(\cos \phi_1 - \cos \phi_3), \\ \sin \phi_2 + \sin \phi_4 &= k(\sin \phi_1 - \sin \phi_3). \end{aligned} \right\} \quad (3)$$

\* For the method, see Riemann-Weber, 'Differential-Gleichungen der mathematischen Physik,' i. p. 334. Forsythe, 'Theory of Functions,' p. 545.



On elimination of  $k$  we have

$$\tan \frac{1}{2}(\phi_2 + \phi_4) = -\cot \frac{1}{2}(\phi_1 + \phi_3). \quad (4)$$

Therefore the middle point of the arc  $(\phi_2\phi_4)$  is separated by a quadrant from the middle point of  $(\phi_1\phi_3)$ . One such arrangement is shown on fig. 1, and in accordance with it we may write

$$\begin{aligned}\phi_1 &= -\alpha, \\ \phi_2 &= -\beta, \\ \phi_3 &= \alpha, \\ \phi_4 &= -\pi + \beta.\end{aligned}$$

When these values are put into the two equations the cosine equation is satisfied identically and the other gives

$$\sin \beta = k \sin \alpha. \quad (5)$$

The two theorems relating to the charge on the planes follow at once from the fact that the difference between the values of the function  $\phi$  at two points on a conductor is proportional to the total charge between the points. So the charges on the four faces are represented by the angular differences as follows :

$$\begin{aligned}\text{AB, } \phi_2 - \phi_1 &= \alpha - \beta, \\ \text{BC, } \phi_3 - \phi_2 &= \alpha + \beta, \\ \text{CD, } \phi_4 - \phi_3 &= \pi + \beta - \alpha, \\ \text{DA, } \phi_1 - \phi_4 &= \pi - \beta - \alpha;\end{aligned}$$

$$\therefore \text{charge on CD} - \text{charge on AD}$$

$$= \text{charge on BC} - \text{charge on AB}.$$

Again, when the breadths of the planes are equal it is obvious from symmetry that  $\alpha$  is a right angle, and therefore

$$\beta = \sin^{-1} k.$$

So we have,

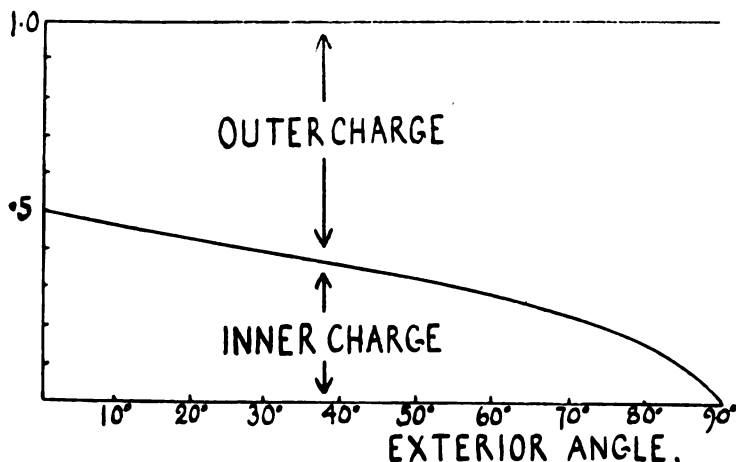
outer charge, on BC and CD : inner charge, on AB and DA

$$= \frac{1}{2}\pi + \sin^{-1} k : \frac{1}{2}\pi - \sin^{-1} k.$$

The graph (fig. 2) shows the partition of the charge between

the concave and convex sides of two equal planes at different inclinations.

Fig. 2.



To return to the differential equation, the relation connecting  $a, b, c, d$  is such as to make the right-hand side a complete differential. On identifying

$$\frac{d}{dx} \cdot (x-a)^{1-k} \cdot (x-c)^{1+k} \cdot x^{-1}$$

with

$$(x-a)^{-k} \cdot (x-b) \cdot (x-c)^k \cdot (x-d) \cdot x^{-2},$$

we find

$$-ka + b + kc - d = 0$$

and

$$ac + bd = 0.$$

The first of these is the relation already given and the second is implied in it, being equivalent to

$$\phi_1 + \phi_3 = \phi_2 + \phi_4 \pm \pi,$$

which is identical with equation (4).

Accordingly we find the integrated equation,

$$z = C\zeta^{-1}(\zeta - e^{ia})^{1+k}(\zeta - e^{-ia})^{1-k} \dots (6)$$

Here  $\zeta = \rho e^{i\phi}$ , where  $\log \rho + \text{const.}$  is the potential and  $\phi = \text{const.}$  is the equation of a line of force. On the planes  $\rho = 1$ , in the field  $\rho < 1$ . The fraction  $k$  is the exterior angle between the planes divided by  $\pi$ , and  $a$  is determined by the ratio of the two breadths in a manner to be found later. It

is convenient to replace the constant  $C$  by  $Ae^{ik\pi}$ , where  $A$  is now a real constant of linear scale. This has the effect of placing the planes symmetrically so that the bisector of their interior angle has the direction of the axis of  $y$ .

For the point  $\phi$  on the equipotential  $\rho$  the equation gives for the modulus and argument of  $z$ ,

$$(x^2 + y^2)^{\frac{1}{2}} = A\rho^{-1} \{1 - 2\rho \cos(\phi - \alpha) + \rho^2\}^{\frac{1}{2}(1+k)} \times \{1 - 2\rho \cos(\phi + \alpha) + \rho^2\}^{\frac{1}{2}(1-k)}, \quad (7)$$

$\tan^{-1}y/x$

$$= k\pi - \phi + (1+k) \tan^{-1}\{(\rho \sin \phi - \sin \alpha)/(\rho \cos \phi - \cos \alpha)\} + (1-k) \tan^{-1}\{(\rho \sin \phi + \sin \alpha)/(\rho \cos \phi - \cos \alpha)\}. \quad (8)$$

The direction of the stream-line  $\phi$  at a great distance from the planes is found by putting  $\rho=0$  in the last equation. The inclination to the  $x$ -axis is then

$$k(2\alpha - \pi) - \phi.$$

To get a set of equally spaced equipotentials  $\rho$  is given a series of values in decreasing geometrical progression. Lines of force can be drawn by joining points with the same  $\phi$  on successive equipotentials.

Fig. 3.

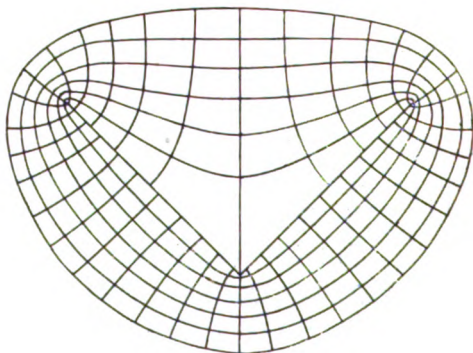


Fig. 3 shows the field for the case

$$k = \frac{1}{2}, \quad \alpha = \frac{\pi}{2}, \quad \rho = .9, (.9)^2 \dots (.9)^6.$$

$\phi$  is taken at  $10^\circ$  intervals.

We come now to the distribution of charge on the planes and the ratio of their breadths. Here  $\rho=1$  and the surface-density,  $\sigma$ , is represented by  $|d\phi/dz|$  which assumes the form

$$\sin^k \frac{1}{2}(\alpha + \phi) \sin^{-k} \frac{1}{2}(\alpha - \phi) (\sin \phi + \sin \beta)^{-1},$$

omitting constants. It will be seen that  $\sigma$  vanishes at A where  $\phi = -\alpha$ , and is infinite at B C D where  $\phi$  has the values  $-\beta, \alpha, (-\pi + \beta)$ , respectively.

For points on CD  $(\phi - \alpha)$  is put for  $(\alpha - \phi)$  and  $\phi$  runs from  $\alpha$  to  $\pi + \beta$ .

It remains to connect  $\phi$  with the distance along the plane measured from the corner.

For  $\rho=1$  the expression on the right of equation (7) becomes for the right-hand plane,

$$4A \sin^{1+k} \frac{1}{2}(\alpha - \phi) \sin^{1-k} \frac{1}{2}(\alpha + \phi).$$

Fig. 4.

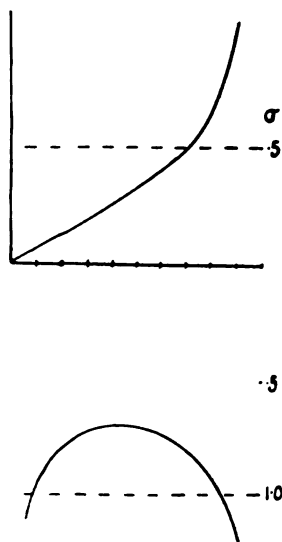
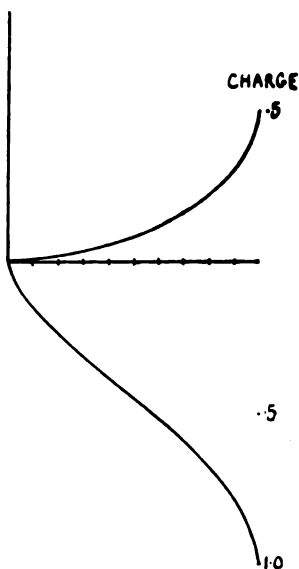


Fig. 5.



By means of these formulæ figs. 4, 5 have been plotted for the special case already dealt with. On fig. 4 is shown the surface density at each point on the two sides of either plane, and on fig. 5 the total charge between the corner and the point.

The breadth of the right-hand plane is obtained by putting  $\phi = -\beta$  in the last formula, which gives

$$4A \sin^{1+k} \frac{1}{2}(\alpha + \beta) \sin^{1-k} \frac{1}{2}(\alpha - \beta).$$

For the breadth of the left-hand plane put  $(\phi - \alpha)$  in the first factor and then  $\phi = \pi + \beta$ , with the result

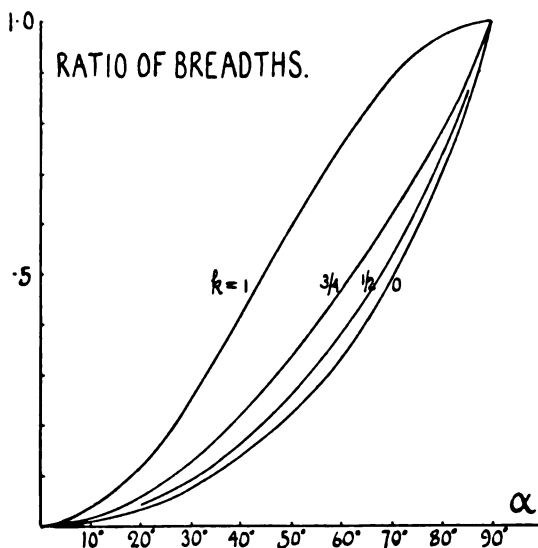
$$4A \cos^{1+k} \frac{1}{2}(\alpha - \beta) \cos^{1-k} \frac{1}{2}(\alpha + \beta).$$

$\therefore$  CB/CD

$$= r = \tan \frac{1}{2}(\alpha + \beta) \tan \frac{1}{2}(\alpha - \beta) \left\{ \frac{\sin(\alpha + \beta)}{\sin(\alpha - \beta)} \right\}^k \quad (9)$$

with  $\sin \beta = k \sin \alpha$ . From this a graph can be plotted for each value of  $k$  from which can be read off the parameter  $\alpha$  to be used for a given breadth-ratio,  $r$  (fig. 6).

Fig. 6.



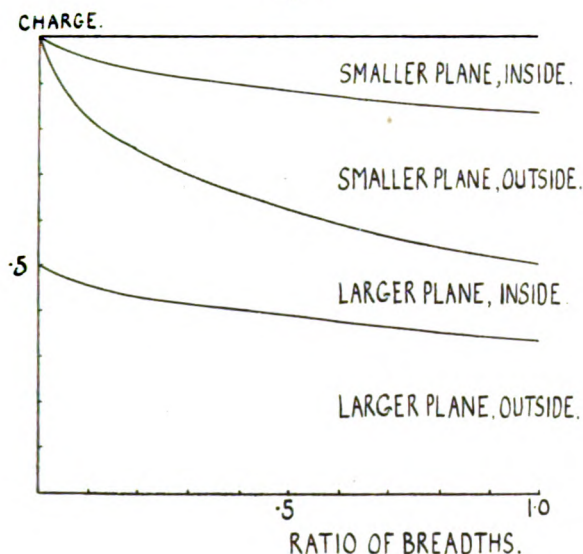
The curves fill the area between the limiting forms for  $k=0$  when  $r = \tan^2 \frac{1}{2}\alpha$  and for  $k=1$  when  $r = \sin^2 \alpha$ , being greatly condensed near the former limit.

When the planes make an obtuse angle, so that  $k < \frac{1}{2}$ , the angle  $\alpha$  is only a little greater than  $2 \tan^{-1} r^{\frac{1}{2}}$ .

Fig. 7 is drawn for two planes at right angles and shows how the total charge is divided into its four parts for

different ratios of the breadths. It will be noticed that the two middle segments together make up half the total charge, in accordance with the first general theorem above.

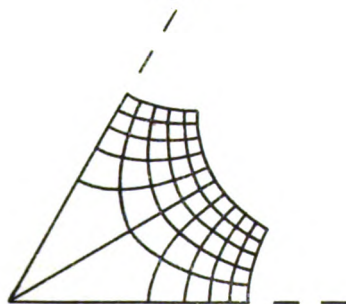
Fig. 7.



*Planes of Infinite Breadth.*

The series of figures 8-13 show a portion of the field at

Fig. 8.



the angle between two charged planes of infinite extent for inclinations of  $60^\circ$ ,  $120^\circ$ ,  $180^\circ$ ,  $240^\circ$ ,  $300^\circ$ , and  $360^\circ$ , bounded by an equipotential and two lines of force. The breadth of

plane taken is the same in each case, and the lines of force divide the charge upon it into five equal parts. The equipotentials correspond to equal differences.

Fig. 9.

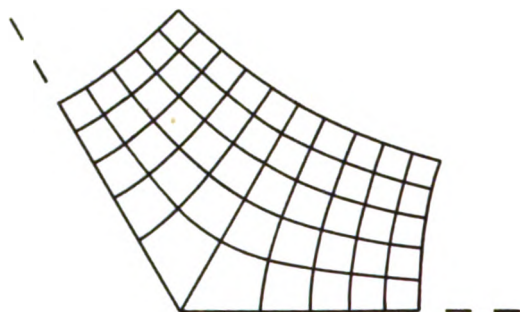


Fig. 10.

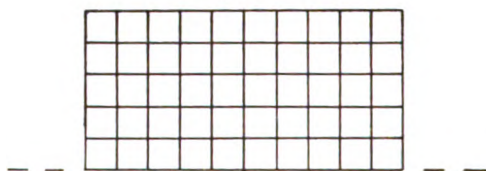
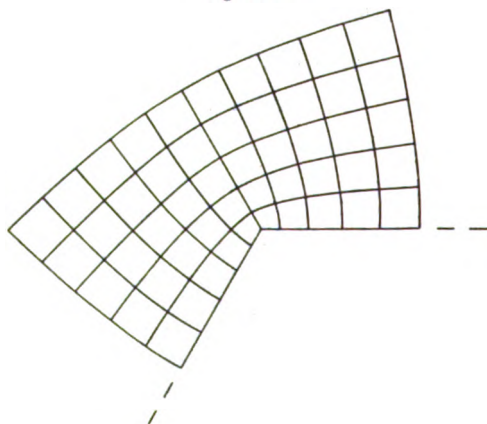


Fig. 11.



The connexion between the inclination  $\alpha$  of the infinite planes and the distribution of charge in the neighbourhood of the hinge is usually stated in terms of the surface-density

Fig. 12.

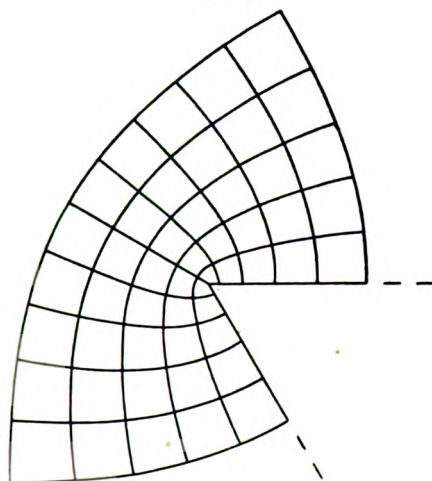
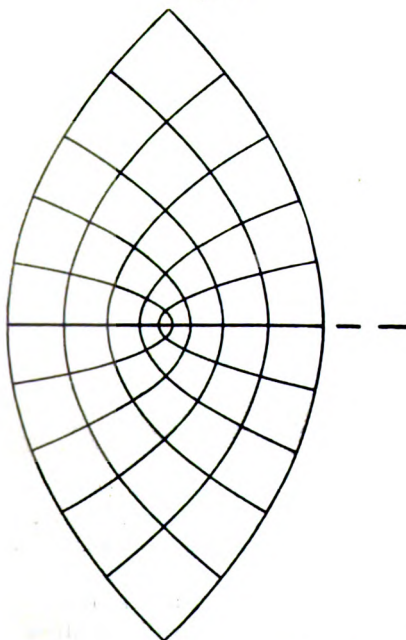


Fig. 13.



which varies as  $r$  to the power of  $\left(\frac{\pi}{\alpha} - 1\right)$ . This does not give a very clear physical conception of the matter, on



account of the infinite value of  $\sigma$  at the edge when  $\alpha > \pi$ . There is an advantage therefore in replacing the surface-density by the charge on a strip of plane of unit length along the direction of the hinge and given breadth. To make a definite comparison between wedges of different angles, we may suppose a fixed charge per unit length,  $Q_0$  say, to reside on a fixed breadth,  $a$ , in every case. Then the charge on breadth  $r$  will be

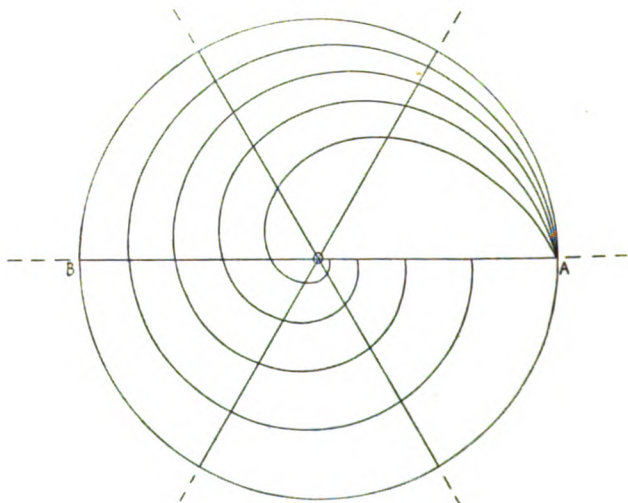
$$Q = Q_0(r/a)^{\pi/\alpha}.$$

So the breadth which carries any charge  $Q$  is

$$r = a(Q/Q_0)^{\alpha/\pi}.$$

When  $\alpha$  is varied the locus of the end of  $r$  is an equi-angular spiral.

Fig. 14.



The diagram fig. 14 illustrates this result. The distances OA, OB are each equal to 25 units. OB is divided into 5 equal parts. A circle is drawn through A and B and spirals through A and the points of division of OB. These will come round and meet OA again at distances 0, 4, 9, 16, 25. Now let OA be kept fixed while another plane, hinged at O, is rotated and let the two planes be charged. Then the circles and the spirals will divide the moving plane, in each position, into parts bearing equal charges.

**XXVII. An Improved All-Metal Mercury-Vapour Pump.** By  
G. W. C. KAYE, O.B.E., M.A., D.Sc., Superintendent of the  
Physics Department, The National Physical Laboratory\*.

A single-stage mercury-vapour pump of the annular-jet type, made wholly of metal, has previously been described in the 'Philosophical Magazine' †. As the result of further experiments, the pump has been considerably simplified in construction and its performance improved. These changes form the subject of this note.

Mercury-vapour pumps have displaced for general purposes almost every other type of high-vacuum pump in the Laboratory. A variety of types are now available, some of them with pumping speeds which, under favourable conditions, are extremely high. To secure this, however, it is usually necessary to have a very efficient backing pump, capable of pressures of the order of a small fraction of a millimetre. What is, however, in our experience, a greater desideratum than high pumping-speed, is for the mercury-vapour pump to be able to function to advantage when the backing-pressure is as high as a few millimetres of mercury, whether owing to a leak or to heavy-gas-emission or to an inefficient backing-pump.

One way of achieving this result is to increase the number of stages in the mercury-vapour pump. Unfortunately, this is very detrimental to simplicity of construction. A single-stage design was therefore adhered to; and the new pump is one which can be made in any good workshop. The advantages of a metal pump have already been touched on in a previous paper ‡.

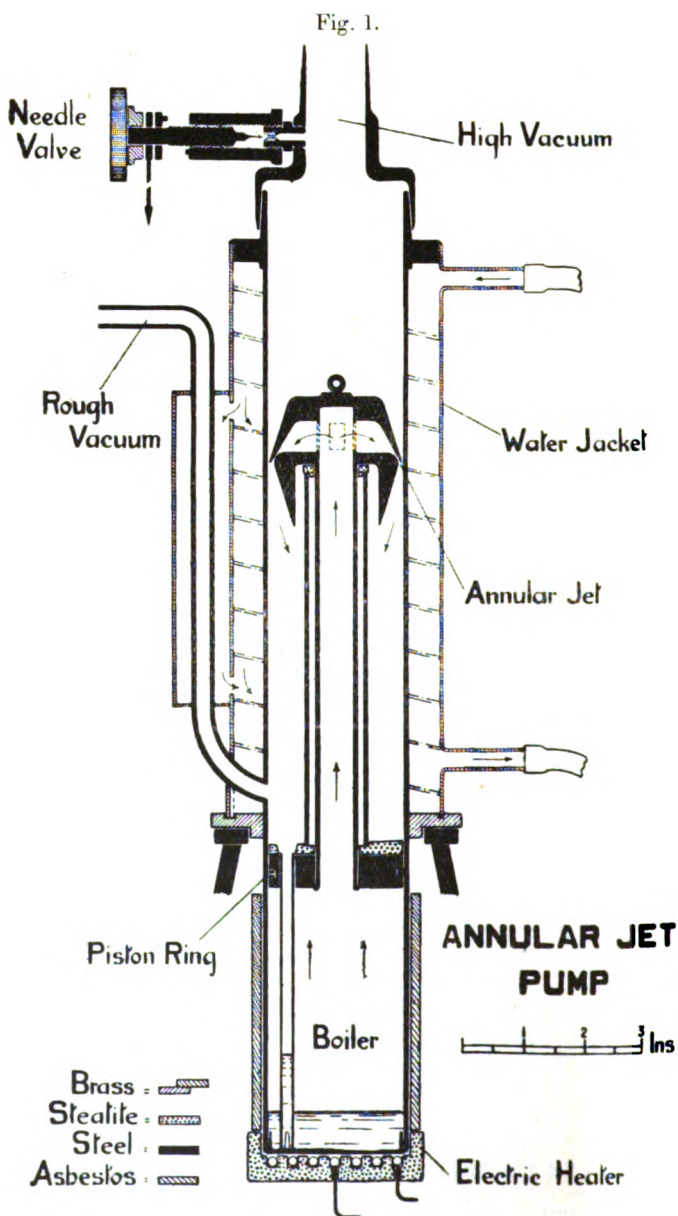
Most of the details of the pump are given in fig. 1, which is almost self-explanatory. The body of the pump is made of solid-drawn steel tubing closed at the lower end. The mercury-vapour is led from the boiler by a central tube to an inverted annular jet situated in the upper water-cooled region.

The thickness of the walls of the tubing is  $1/16$  inch. The bottom of the boiler, which is of the same thickness, is welded to the walls. The top of the boiler is sealed by means of a "Clupet" piston ring; and the ring is "lapped in" much as is a ring in the cylinder of an engine, any scale being first removed. The boiler-top is thermally insulated above by a disk of baked steatite, the upper surface of which

\* Communicated by the Director.

† Backhurst & Kaye, Phil. Mag. xlvii. p. 1016 (May 1924).

‡ Backhurst & Kaye, Phil. Mag. xlvii. p. 918 (May 1924).



is inclined so as to assist the condensed mercury to find its way back to the boiler by the return tube. Baked steatite is also used to insulate and support the tube which jackets the central vapour-tube.

Attention was paid to the shape of the two deflectors enclosing the annular jet to secure favourable expansion conditions for the jet. The widths of the jet and of the adjacent "diffusion annulus" are each  $1/32$  inch. A uniform diffusion annulus is secured by leaving three small outward projections equally spaced on the lip of the upper deflector. The boiler-top, the central vapour-tube, and the jet-system form a unit which can be readily withdrawn from the pump for examination.

The pump is cooled by a closed water-jacket, either of brass (as shown) or steel with welded flanges. A helix of copper tape inserted in the jacket causes a swirling action of the water, the cooling being very efficacious. The water-jacket is extended some distance above the jet, so that, although the new design utilizes a greater boiler-pressure and a higher jet-velocity, there is, as compared with the old design, a marked diminution in the amount of stray mercury-vapour which finds its way to the high-vacuum side of the pump.

The improved thermal insulation of the boiler-top also permits the extension of the water-jacket almost to the level of the boiler-top, thus considerably augmenting the condensation-space below the jet, without any increase in the overall length of the pump.

The upper end of the pump is closed with a steel cap fitted with a ground joint. A second ground joint forms the connexion between the steel cap and the glass connecting-tube of the apparatus to be exhausted. The use of sealing-wax as in the older design is thus obviated. Our experience is that such steel-to-steel and steel-to-glass joints up to  $2\frac{1}{2}$  inches diameter are trustworthy and practicable for vacuum work. The merest trace of grease is necessary. We have found a taper of  $4^\circ$  (between sides) to have advantages and have accordingly adopted it as standard, so as to secure interchangeability of apparatus. Suitable mercury-sealing troughs are readily incorporated in the design if it is desired to avoid the use of grease in the ground joints.

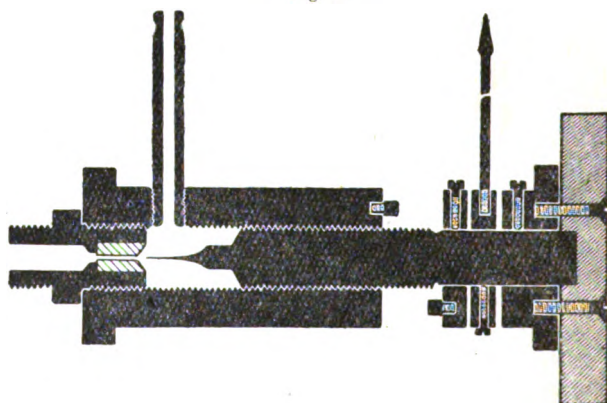
Either electric or gas heating may be employed. Six hundred watts or twelve litres of coal-gas per minute can be utilized without overheating. A backing-pressure of 4 to 5 mm. is sufficient for most purposes, and the highest

### 352 *An Improved All-Metal Mercury-Vapour Pump.*

vacua may be attained with a backing-pressure of  $1\frac{1}{2}$  mm. The amount of mercury in the boiler is 50 c.c.; and, as a result of the reduced thermal capacity, the pump, using gas heating, will operate within three minutes from cold. It may perhaps be added that, if full advantage is to be taken of the high speed of the pump (which somewhat exceeds that of the earlier model), there should be no constriction anywhere in the high-vacuum system, and the backing-pump should be fully capable of keeping pace with the mercury-vapour pump.

A useful addition is a micrometer needle-valve for regulating the degree of the high-vacuum by means of an adjustable air-leak. The needle-valve, which is conveniently mounted in the side of the upper cap, is illustrated in fig. 2. It consists essentially of a steel needle which

Fig. 2.



#### MICROMETER NEEDLE VALVE.



partially or completely closes a small circular hole in a brass plug. The steel needle is conveniently turned from the solid as part of a steel spindle, from which it projects. The needle proper is about 8 mm. long and tapers slightly from a maximum diameter of a little more than  $\frac{1}{2}$  mm. The hole in the brass plug is 5 mm. long and  $\frac{1}{2}$  mm. in diameter throughout.

About 5 mm. of the spindle next to the needle is reduced in diameter, so that, even in the closed position of the valve, the "leakage tube" to the air is uninterrupted. The main body of the spindle is 8 mm. in diameter and is provided over about  $2\frac{1}{2}$  cm. of its length with a micrometer-thread of  $\frac{1}{2}$  mm. pitch. If rubber grease is employed as a lubricant, the length of screwed thread on the spindle is such as to obviate any need for a gland or seal.

The brass plug which forms the valve-seating is mounted in a steel tube, which connects the valve with the cap of the pump.

The needle readily beds itself into the brass seating, and very little pressure is needed to close the valve completely. To prevent the needle from damaging the seating by being forced beyond the closed position, an adjustable stop is provided. This may be disengaged if it is desired to open the valve more than a complete turn.

I wish to acknowledge the effective assistance given by Mr. W. H. Sewell and Mr. J. Balmano, of the Observer staff of the Laboratory. The work was carried out partly in connexion with the programme of the Radio Research Board of the Department of Scientific and Industrial Research.

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XXVIII. *An Investigation into the Theory of the "Three-Point Gap."* By C. E. WYNN-WILLIAMS, M.Sc., Fellow of the University of Wales, University College of North Wales, Bangor\*.

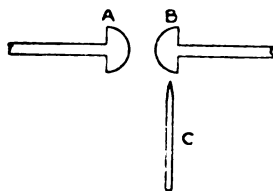
**A**LTHOUGH the phenomenon termed the "three-point effect" has been known for some time, and has been utilized in the construction of a form of standard spark gap, very little attention appears to have been paid to its theory. As far as the writer is aware, no theory, up to the time of writing, has been put forward which explains the effect completely.

The phenomenon is as follows. Let A B (fig. 1) be the two electrodes of a spark gap connected to an induction coil or other impulsive high potential apparatus. Corresponding to any given set of conditions, there will be a certain maximum length of gap, depending upon the peak voltage of the coil, the dimensions of the electrodes etc., for which

\* Communicated by Prof. E. Taylor Jones, D.Sc.

a spark can pass regularly. If the gap is made of slightly greater length than this, the other conditions remaining the same, the spark will not pass. If, however, a third pointed electrode, C, is brought near one of the main electrodes, it is found that, under certain conditions, the spark will again pass regularly across A B, while a small spark passes from the third electrode to the neighbouring main electrode. This small spark is called the "pilot," "teaser," or "trigger" spark.

Fig. 1.



The pilot spark thus virtually lowers the impulsive sparking voltage of the main gap. Moreover, it appears to render the sparking in that gap more regular than in the ordinary two-electrode gap, so explaining the use of the "three-point gap" as a standard.

Two explanations of the phenomenon have been suggested. According to the first, ions are produced by the small pilot spark, which, travelling into the main gap, facilitate the passage of the main spark. According to the second, the pilot spark sets up oscillations in the main electrodes, which serve to cause the peak voltage periodically to rise above the critical sparking voltage, and so cause the main spark to pass.

As neither explanation appeared to have been fully investigated, it was decided to conduct experiments which, it was hoped, would establish one or other of them, or, alternatively, provide evidence on which a new theory could be founded.

The first experiments carried out were of the nature of qualitative tests to collect information as to the conditions under which the effect could be obtained.

The apparatus consisted of an ordinary two-electrode spark gap having zinc electrodes, about two centimetres in diameter and hemi-spherical\* in shape. These were

\* The main electrodes of the standard three-point gap are usually sharp points. As, however, it was found that the three point effect was much more marked when rounded electrodes were used for the main gap, together with a sharp point for the third electrode, the experiments subsequently described were carried out with this type of gap.

connected to the terminals of a small induction coil which gave a steady stream of sparks four or five millimetres in length. The length of the gap was so adjusted that the spark just failed to pass. The third point consisted of a sharp sewing-needle attached at its centre to an insulating handle of sealing-wax. It was observed that when the point of this was brought sufficiently near one of the main electrodes for a small pilot spark to pass, the three-point effect was obtained (*i. e.*, the main spark passed regularly). Moreover, it was observed that it was possible to obtain the effect when the point (and pilot spark) were moved to the extreme end of one of the main electrodes—about four inches from the main gap. It was also found possible to obtain the effect when the point was near the gap, but not sufficiently near either of the main electrodes for a pilot spark to pass, and, under certain conditions, when the point was allowed to touch one of the main electrodes. It did not seem to make any appreciable difference to which of the main electrodes the point was approached, unless one of them was earthed, in which case the point had to be brought near the other electrode.

These preliminary tests tended to the view that the phenomenon was dependent, not so much on the pilot spark (for it could be obtained without a pilot spark) as on some property of the third electrode.

Experiments made with a blunt third electrode showed that the effect was not obtained so easily as in the previous case. This appeared to indicate that a silent discharge from the third electrode might be responsible for the phenomenon in the case where it was obtained without a pilot spark.

Further experiments with an electrode sharpened at both ends tended to support this view, for it was observed that when any sharp point from which a silent discharge took place was within about five or six centimetres of the main gap, and "visible" \* from it, the main spark passed regularly. This is illustrated in fig. 2, where A and B represent the main electrodes, E the main gap, and C D the third electrode, pointed at both ends.

In case (*a*), the main spark was found to pass when C was brought sufficiently near to B for either (1) a pilot spark, or (2) a silent discharge, to pass from B to C, and be visible from E. If, however, C touched B, the effect ceased. In this case, D was too far from E for the silent discharge from it to affect the main gap.

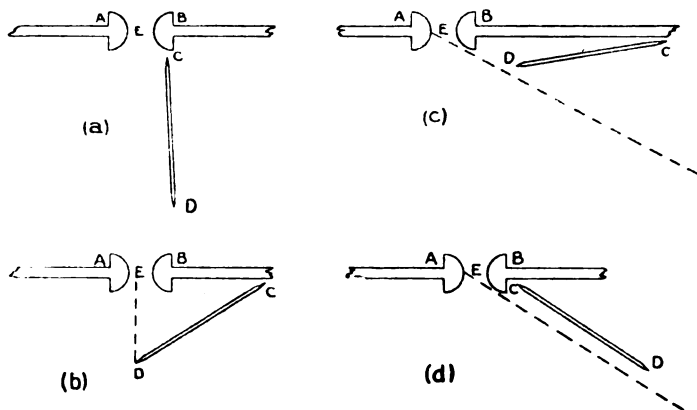
\* By "visible" is meant that a straight line, clear of all objects, could be drawn through the air from the point to the gap.



In case (b), the effect could be obtained when D was within five or six centimetres of the main gap, and (1) C touched B, (2) C was sufficiently near B for a pilot spark to pass, or (3) C was sufficiently near B for a silent discharge to pass. Here, it was the *secondary* silent discharge, at D, that was visible from E.

In cases (c) and (d), the main spark could not be made to pass under any circumstance, both discharges (at C and D) being invisible from the gap.

Fig. 2.



It was observed that if the end C of the conductor in case (a), and the end D in case (b), was covered with wax, the main spark would not pass.

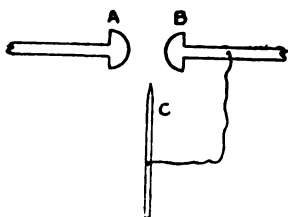
The conclusion to be drawn from these experiments appears to be that some form of discharge (silent or spark) must take place within a certain distance (about six centimetres in this case) of the main gap, and be visible from it, before the three-point effect can be obtained\*.

To investigate the action of the discharge in greater detail, the apparatus was modified slightly. As the effect could be obtained (case (b)) with one end of the third electrode in contact with the main electrode, in the experiments that followed, a sharp needle, connected to one of the

\* This view is supported by an observation made by Dr. J. D. Morgan ('Principles of Spark Ignition in Internal Combustion Engines,' p. 61). He finds that when the insulation of the gap is damp, the surface discharge to the earthed support is effective in lowering the impulse ratio of a two-electrode gap, but only when the discharge is on the gap side of the support (i.e., presumably when the discharge is "visible" from the gap).

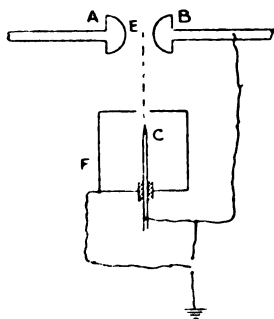
main electrodes, was used instead of the previous third electrode. This arrangement (fig. 3) produced the effect when the point was within five or six centimetres of the gap, and was found to be much more convenient in use than the previous third electrode. The experiments were afterwards repeated with another type of third electrode, which gave a pilot spark instead of a silent discharge (see p. 367).

Fig. 3.



The apparatus was set up in a dark room, and the point C carefully observed while it was brought near the gap. It was found that the main spark commenced to pass while there was yet no visible glow around the point C. When, however, C was brought nearer to the gap, a violet glow appeared. A small piece of wax placed on the end of the point was found to stop both the glow and the three-point effect, thus strengthening the view that the silent discharge from the point was necessary. This experiment was varied

Fig. 4.



by surrounding the point with a small metal chamber F (fig. 4), closed except for a small aperture so arranged that the point was visible from the gap. The chamber could be connected to earth, or to the same electrode as the point. The length of the gap was adjusted as usual to just above

the critical spark length, the chamber being connected to earth. With the point connected to the main electrode, the main spark passed regularly, showing that the phenomenon was obtained. The experiment was then repeated with the chamber connected to the same electrode as the point. It was found that the spark now failed to pass. In the first case, a silent discharge passed from the point to the earthed chamber, whereas, in the second, the point and the chamber being at the same potential, no such discharge was possible.

The fact that the three-point effect could be produced by a silent discharge as well as by a spark showed that the phenomenon was not caused by oscillations set up in the main electrodes by the pilot discharge, for such oscillations could only have been produced by the pilot discharge when the latter was a spark. The silent discharge would behave as a high resistance leak, and would give rise to no such oscillations.

The effect of interposing thin sheets of various substances between the point and the gap was next investigated. It was observed that a thin sheet of any of the substances tried (with one exception) had the effect of screening the gap from the action of the point, and so causing regular sparking at the main gap to cease. The only substance tried which was found not to cut off the effect but to be "transparent" to it, was a celluloid film, so thin as to give interference fringes when viewed by monochromatic light. Such a film was formed by allowing a few drops of a dilute solution of celluloid in amyl acetate to fall on a clean water surface and to evaporate. When such a film was picked up by means of a wire ring and allowed to dry, it was found not to cut off the three-point effect when interposed between the point and the gap\*.

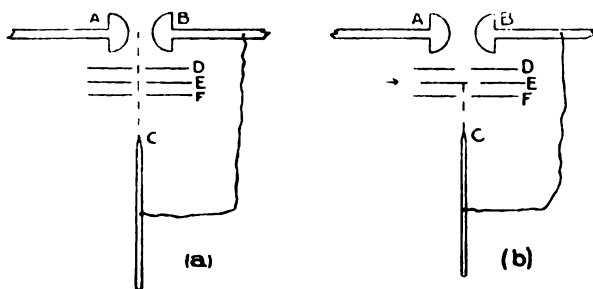
Amongst the substances tried which were found to be "opaque" were glass, quartz, mica, wood, ebonite, paper, cardboard, paraffin wax, soap films, gold leaf, metal foils and plates, etc. A small hole in any of these substances, however, would allow whatever caused the effect to pass through, provided the point, the hole, and the gap were in a straight line. It was also observed that when the screen was introduced gradually, the spark in the main gap ceased passing regularly as soon as the edge of the substance intercepted the line joining the point and the gap. These two observations seemed to indicate that as long as some part of the gap was visible, and unscreened from the point,

\* Another method of producing these films is described in 'Discovery,' p. 133, April 1925.

the main spark passed regularly, and the following more elaborate experiment confirmed this.

Three small mica screens D, E, F, each perforated by a small hole, were interposed between the point and the gap and so arranged that the point, the apertures, and the gap were in alignment (fig. 5 a). The "effect" was found to penetrate through the apertures to the gap and render the sparking there regular. The centre screen, E, was then slightly displaced, so that its aperture was no longer in alignment with the others (fig. 5 b). The main spark failed to pass, showing that whatever previously affected the point could not travel from the point to the gap on account of there being now no straight line path for it. By removing

Fig. 5.



screen E, the two remaining screens with their apertures served to form a "beam" of what travelled from the point, and by displacing the system slightly, the beam was made to just miss the gap. In this case also, the main spark ceased to pass regularly.

It was evident, then, that something produced by the silent discharge travelled in straight lines from the point to the gap and so affected conditions there as to facilitate the passage of the main spark. The following explanations as to the manner in which this might have been accomplished suggested themselves:—

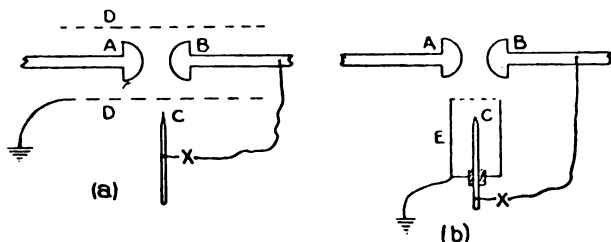
(1) The charged point, or the silent discharge, might have affected the electric field in the vicinity of the gap.

(2) Ions produced by the discharge might have travelled to the gap and so facilitated sparking there—a modification of the original explanation which assumed the ions to be produced only by the *pilot spark*.

(3) Some form of radiation might have been emitted by the discharge, which, travelling to the gap, ionized the gas there, or produced photo-electric effects at the electrodes.

With regard to (1), it is significant that very thin films of *both conductors and non-conductors* (with the one exception) cut off the effect when interposed between the point and the gap, and further, that a small hole in any of them would allow the effect to pass when the point, the hole, and the gap were in alignment. It is extremely improbable that such complete cutting off would have been obtained in all cases had the effect been due to any disturbance of the field. The following experiments, however, show that the three-point effect is obtained when the field is *not* disturbed.

Fig. 6.



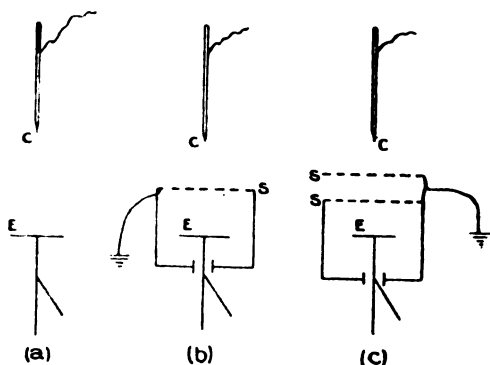
A cage of fine wire gauze, D (fig. 6 *a*), was constructed so as to surround the gap, A B, and was connected to earth. The third electrode, C, which could be connected to, or disconnected from, B, at the point marked X, was brought near the cage, and within a few centimetres of the gap. With the connexion at X broken, the coil was started and the gap length adjusted to just above the critical spark length. The connexion was then made at X, and it was observed that the main spark passed regularly. In this case, the field near the gap, being within the earthed cage, could not have been disturbed by external conditions.

The point C was then placed within, and insulated from, an earthed metal chamber E (fig. 6 *b*), having a gauze window facing the gap. The point (and chamber) was brought to within a few centimetres of the gap, and the latter adjusted as before. When connexion was made at X steady sparking resulted at the main gap. In this case, the point being within an earthed metal chamber, the only change in the electric field occurring on making connexion was within the chamber itself.

As the three-point effect was obtained in both cases despite the fact that the field near the gap was not disturbed, it is evident that disturbances occurring in the field near the gap are not necessary for the production of the phenomenon.

As regards (2), the fact that almost all substances cut off the effect completely when interposed between the point and the gap, and that ions of the same polarity as the point were liberated from the latter during the silent discharge (as could be shown by the diverging of the leaves of an electroscope brought under the point) were consistent with this view. On the other hand, as it seemed natural to conclude that the ions travelled along the lines of force radiating from the point to the electrodes of the main gap, and as the point was connected to one of the electrodes, so that these lines of force were not evenly distributed, it seems difficult to reconcile this view with the "straight line propagation" effect observed. Again, a sheet of earthed metal gauze interposed between the point and the gap, as shown in the previous experiments, allowed the point to affect the main gap. Such a screen, however, would considerably alter the distribution of the field between the point and the gap, and (if the A electrode of the gap were earthed) even reverse the direction of it, which, of course, would tend to drive ions away from the gap.

Fig. 7.



To investigate this matter further, and to ascertain whether and under what conditions ions could penetrate a gauze screen, the following tests were carried out.

The third point C was placed about six centimetres (this being the "range" of the point for the three-point effect) above the cap of an electroscope E (fig. 7 a). On starting the coil, the leaves of the electroscope diverged, thus showing that ions travelled from C to E and charged the electroscope. This was found to be the case whether C was connected to electrode A or B of the main gap. An earthed sheet of

metal gauze S was then interposed between C and E, and the experiment repeated. It was observed that a very slight deflexion was obtained. Suspecting that this was caused by ions travelling from C to E along lines of force round the edge of the gauze, an earthed metal collar was placed round the cap of the electroscope, and the experiment repeated with the gauze placed on this (fig. 7 *b*). It was now observed that the electroscope remained uncharged, showing that ions did not traverse the region of no field existing between S and E.

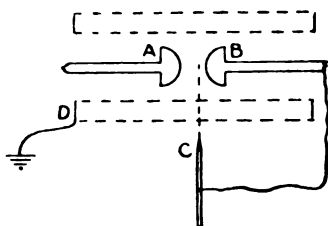
On trying this with E initially charged (so that a field existed between E and S, which was at zero potential), it was observed that : (1) If the charge on E was of the same sign as that on C, nothing happened (*i. e.*—the field between E and S, being opposed to that between C and S, ions were prevented from reaching E and altering its charge) ; and (2) If the charge on E was of the opposite sign to that on C, the leaves of the electroscope fell, and did not rise again. In case (2), the field between E and S being now in the same direction as that between C and S, the ions from C, on reaching S, were driven to E under the action of the field between S and E. Having reached E, the charges on the ions, being of opposite sign to the initial charge on E, neutralized part of the latter (as indicated by the fall of the leaves), so gradually reducing the field between S and E to zero. Then, as before, no further ions passed through S to E, as was shown by the leaves remaining undeflected.

Evidently, then, an earthed gauze screen prevented the passage of ions from C to E, provided there was either (1) no field, or (2) an opposing field, on the side furthest from the point. A double screen, constructed from two sheets of earthed gauze separated by an interval (in which no field could exist as both sheets would be at the same potential), should therefore prevent the passage of ions in all cases. This was shown to be the case, for, by placing such a screen between the point and the electroscope (fig. 7 *c*), it was observed that whatever was the original condition of E (uncharged, or charged positively or negatively) ions from C now failed to reach E and alter its charge.

A "double cage" of earthed gauze D was constructed so as to surround the gap (fig. 8), the distance between the two cylinders being about one centimetre. With this arrangement, it was observed that the point C, placed just outside the cage, could produce the three-point effect just as readily as when the cage was absent, thus showing that the passage of ions into the gap is not essential for the production of the phenomenon.

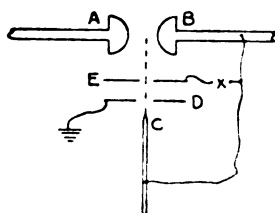
Making use of the second condition under which ions could be prevented from reaching the gap (i. e., an opposing field), the following experiment was carried out. Two

Fig. 8.



small metal plates D and E (fig. 9) separated by a distance of about a centimetre, and having a small hole bored in each, were arranged between the third point C and the gap so that the point, the holes, and the gap were in alignment. Plate D (nearest the third point) was earthed, while E could be connected to or disconnected from the third electrode at the point X. By this means, when E and C were connected, so that they were at the same potential, a field was set up between D and E in the opposite direction to that existing

Fig. 9.



between C and D. As was shown in the previous experiments, such a field would prevent ions from C from reaching the gap. The connexion at X being broken, the third point was found to render the passage of the main spark regular. The connexion was then made at X, and no difference was observed in the regularity of the passage of the main spark. This seems to indicate, as before, that the three-point effect is independent of the passage of ions from the point to the gap.

Two other observations tend to confirm this view. In the first place, when the gauze screen S (fig. 7 b) was replaced by the celluloid film already referred to (which did not cut



off the three-point effect), it was observed that the electro-scope E retained its charge (+ or -), showing that such a film, while allowing the point to affect the gap, effectively stopped the passage of ions. Secondly, while the third point could only produce the phenomenon when within about six centimetres of the gap, it was observed to be capable of producing a deflexion of the leaf of an electro-scope placed as far away as eighteen centimetres. If, therefore, the effect had been due to ions, the point should have been capable of producing the three-point effect at greater distances from the gap than six centimetres. Further experiments with a different type of third electrode referred to later (see page 368) tended to confirm this view.

As, therefore, neither ions travelling into the gap nor disturbances of the electric field in its vicinity seemed to be necessary for the production of the phenomenon, there remained to be investigated the possibility that it was due to some radiation emitted from the point, which either ionized the gas in the gap, or caused photo-electric effects at the electrodes.

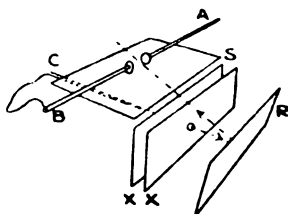
It had already been observed that whatever travelled from the point to the gap did so in straight lines, a fact which, with the screening effect obtained, was consistent with the view that it was a form of radiation. Tests were then conducted to ascertain whether it was capable of the reflexion and refraction effects usually associated with radiant energy. Great difficulty was, however, experienced at this stage of the work owing to the fact that the maximum distance that could be obtained between the third point and the gap was only six centimetres, and that all the experiments had to be carried out in this space.

As regards refraction, it was out of the question to ascertain whether the radiation obeyed Snell's law, as the only substance which was found to be transparent was, as explained, a thin celluloid film, of a thickness which gave interference fringes with monochromatic light.

The test for reflexion the experiment illustrated in fig. 10 was arranged. A and B were the main electrodes, and C the third point connected to B, and placed under the gap, pointing in a direction perpendicular to the line joining A and B. S was a screen so arranged that no "radiation" could pass directly from C to the gap, while XX were two perforated mica screens which served to direct the "radiation" into a "beam." The coil was started, and the gap adjusted to just above the critical spark length. When S was not in position, regular sparking was obtained in the

gap owing to the direct effect from the point C. The sparking ceased when S was placed in position, but recommenced when a polished glass plate R was brought near the point and so adjusted as to "reflect" the "beam" falling upon it into the gap. It was observed, however, that while reflexion results were obtained consistent with the presence of radiation, the reflexion was diffuse, and not regular. For the angle at which the mirror was held could be varied over a region on either side of the value necessary had the angle of reflexion been equal to the angle of incidence. Various substances were tried as mirrors—glass, quartz, polished metal plates, paper, cardboard, etc., and the same diffuse reflexion effects obtained from them.

Fig. 10.



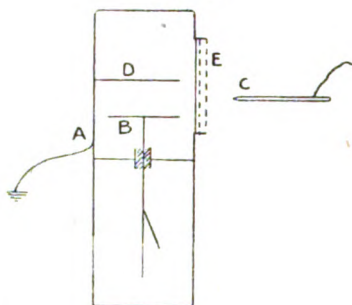
The effect seemed to be independent of the condition of the surface of the mirror,—a piece of paper held in a suitable position caused the main spark to pass just as readily as a piece of polished glass. In no case was any reflexion other than "diffuse" obtained.

As the only transparent substance was very thin celluloid, and only diffuse reflexion effects were obtainable, the radiation could not be focussed by either lenses or mirrors. Also, as the methods usually employed for determining wave-lengths utilize either reflexion or refraction effects for obtaining a double image or a spectrum, it was equally impossible to measure the wave-length of the "radiation" in the ordinary manner.

To ascertain whether the radiation ionized the air through which it passed, a simple ionization chamber was constructed as shown in fig. 11. This consisted of an earthed metal chamber A, in which was placed the electrode B of a small gold-leaf electroscope. Above and near to this was a parallel plate D, attached to the chamber. A window E, covered with a thin celluloid film and a double earthed gauze (as used in a previous experiment), while allowing

the radiation from the third point C to enter the chamber, prevented the entry of any free ions. The electroscope was charged, and the rate of fall of the leaf due to leakage was observed. The electroscope was then recharged, and the coil started so as to maintain a silent discharge from C. It was observed that, in the several experiments performed, the rate of fall of the leaf was from four to sixteen times greater (depending upon the conditions of the experiment) when the radiation was allowed to enter the chamber than when a screen was interposed between C and E, thus showing that the radiation ionized the air in the space between B and D and so increased the rate of leakage of the charge. As the

Fig. 11.



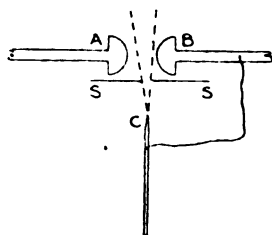
rates of fall of the leaf for positive and negative charges on the electroscope were observed to be approximately the same, it was concluded that if the radiation produced any photo-electric effects, they were small compared with its ionizing properties, for had there been any marked photo-electric effect, the rate of fall of the leaf should have been expected to be different for a negative charge on the electroscope and for a positive charge.

This is supported by the fact that the pressure in the chamber of a small amount of turpentine vapour (which is strongly ionized by "Entladungstrahlen"), increases the ionization.

The radiation being thus proved capable of ionizing the air through which it passed, the following experiment was arranged (fig. 12). The third point and the gap being set as usual, the three-point effect was obtained. In accordance with the straight line propagation effect observed, two screens SS were then placed between the point C and the gap, so as to shield the electrodes from the point, and leave exposed only a small section of the gap (*i. e.*, the gas) to

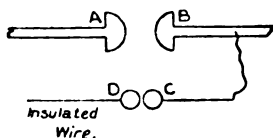
the radiation from C. It was observed that this did not affect the regularity of the passage of the main spark. As by this means ionization effects only could be obtained in the gap, it was concluded that photo-electric effects were not necessary for the production of the three-point effect, and that it was due to the ionization of the gas in the gap by the radiation emitted from the point.

Fig. 12.



So far, only one type of discharge had been investigated (viz., the silent discharge). As in certain cases the three-point effect was caused by a pilot spark visible from the gap, it remained to investigate whether the conclusions drawn for the silent discharge applied also to the spark. For this purpose, the third electrode was altered as shown in fig. 13.

Fig. 13.



A and B, as usual, were the main electrodes, set apart at just above the critical spark length, while C and D were two small spheres, about three millimetres in diameter, and separated by about half a millimetre. C was connected to the main electrode B, and D to a short length of wire. The capacity of the latter was sufficient to enable a small spark ("pilot spark"), visible from the main gap, to pass across C D when the potential rose across A B. By increasing the length of the free wire, the intensity of the pilot spark could be increased. With this arrangement, the experiments carried out with the pointed type of third electrode were repeated (with the exception, of course, of those peculiar to the silent discharge), and it was observed that *the general*

*conclusions drawn for the silent discharge applied also to the spark discharge.* Moreover, the radiation from this pilot spark was found to be more intense than that emitted from the silent discharge, for while the maximum distance that the point could be placed from the gap and cause the effect was only six centimetres, the pilot spark could produce the three-point effect when ten centimetres from the gap.

On bringing an uncharged electroscope near to the pilot spark gap, to investigate whether ions were liberated as in the case of the silent discharge, it was observed that the leaves were not deflected even when the cap of the electroscope was within one or two millimetres of the gap—*i. e.*, just too far away for a spark to pass to the electroscope. (In the case of the silent discharge, it will be remembered that the leaves of the electroscope were deflected when the cap of the latter was as far away from the point as eighteen centimetres.) The conclusion was therefore drawn that either (1) no ions, or (2) an equal number of + and - ions were propagated from the pilot spark to the electroscope. As, however, owing to the way in which the pilot gap was connected (*i. e.*, one electrode of the pilot gap to one terminal of the coil, the other being free) there would be an effective field between the gap and the electroscope (initially at zero potential) which would tend to deflect + and - ions in different directions, the second conclusion is extremely unlikely. This experiment therefore confirms the view that the phenomenon is not dependent upon the passage of ions into the gap (see page 364).

An interesting observation was made when the screening tests carried out in the case of the pointed third electrode were repeated with the pilot gap in place of the point. It was found that a thin plate of quartz, when interposed between the pilot spark and the main gap, while considerably reducing the regularity of the passage of the main spark, did not cut off the three-point effect completely. When, however, the electrodes of the main gap were shielded from the action of the radiation from the pilot spark, as described in a previous experiment, it was observed that the three-point effect was completely cut off by the quartz. The conclusion was therefore drawn that in the case of the pilot spark, which was rich in ultra-violet light, although the radiation ordinarily producing the ionization in the gap was cut off by the quartz plate, sufficient ultra-violet light was transmitted by the latter to cause appreciable photo-electric effects at the electrodes of the main gap, and thus maintain the slight three-point effect observed.

In the case of the silent discharge, it will be remembered, quartz was found to cut off the effect. As ultra-violet light is to be expected from this type of discharge also, the screening tests were again repeated, with a very intense silent discharge, and the distance between the point and the gap reduced to about three centimetres. In this case, it was found that a quartz plate would permit sufficient ultra-violet light from the silent discharge to reach the electrodes and so maintain a very slight three-point effect. As before, however, when the electrodes were shielded, the effect was completely cut off by the quartz.

These experiments show that the photo-electric action of the ultra-violet light emitted from an intense pilot discharge (spark or silent), while not being the main cause, assists in the production of the three-point effect.

In the case of the pointed third electrode, it was also found possible to obtain the three-point effect by connecting the sharp point to one terminal of a wimshurst machine instead of to one of the main electrodes. When the potential at the point was thus raised sufficiently high for a silent discharge to take place at the point, it was observed that the main spark commenced to pass regularly as usual. With the other "pilot gap" type of electrode (fig. 13) the three-point effect could only be obtained when the necessary potential for the production of a pilot spark was derived either from the coil supplying the main gap, or from another coil operated from the same break as the main coil. In these cases, the passage of the pilot spark was simultaneous with the rise of potential across the main gap.

Having thus traced the main cause of the three point phenomenon to the ionization produced in the gas in the main gap by the radiation emitted from the pilot discharge, it remained to identify (if possible) the radiation. As it was out of the question, for reasons already stated, to measure its wave-length in the ordinary manner, its position in the general wave spectrum had to be inferred from its observed properties. These were:—

- (1) The radiation, while capable of diffuse reflexion effects, could not be regularly reflected.
- (2) It ionized the air through which it passed.
- (3) It was transmitted by a thin celluloid film, but not by any other substance tried.
- (4) It could penetrate air at ordinary pressure to a distance of some centimetres.

Fig. 14 is a diagram representing the general wave-spectrum, in which the wave-lengths are plotted logarithmically in the vertical direction, and the approximate regions of the various known types of radiations indicated by horizontal lines. Two sections in the diagram—B, from a wave-length of 1·8 millimetres to about 0·4 millimetre, and G, from a wave-length of about 1000 Å. to approximately 13 Å., call for special attention. The type of radiation corresponding to B has been produced experimentally, although its properties have not yet been completely investigated. From the fact, however, that the properties of radiations A and C, on either side of it, are very similar, it is reasonable to conclude that the properties of radiations B do not differ greatly from them. With regard to G, an extensive section, the only known types of radiation existing in it are the “entladungstrahlen” discovered by Wiedemann\*. Owing to the difficulties encountered in the experimental work, the properties of these radiations have not yet been fully investigated, but the following have been established:—

- (1) They are not capable of being reflected regularly.
- (2) Gases through which they pass are ionized by them.
- (3) A thin celluloid film is transparent to them while most other substances are not.
- (4) They penetrate air at ordinary pressure to a distance of some centimetres.
- (5) They are emitted by spark, and the luminous parts of low pressure, discharges.
- (6) The rays can produce “thermoluminescence” in certain “solid solutions.”

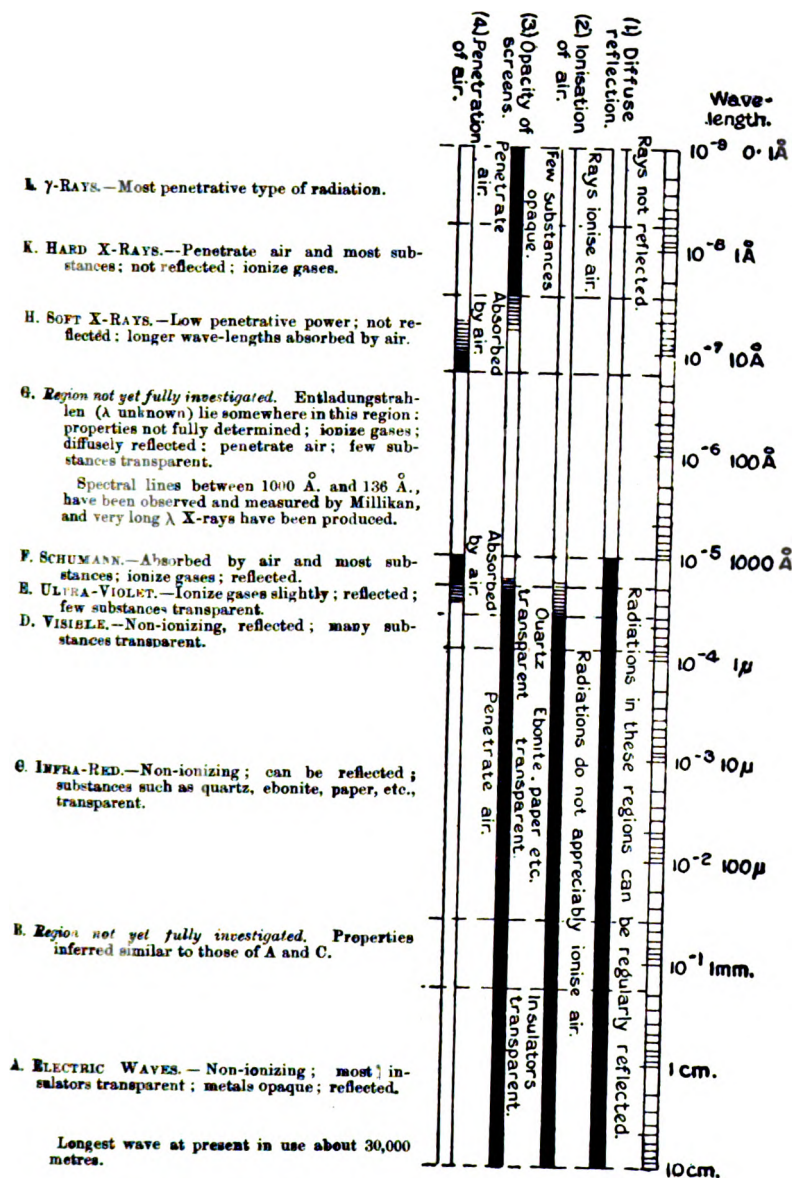
The properties of the radiations in the remaining sections are sufficiently well known, and need not be set down here.

Making use of the four properties specified for the radiation now considered, in the light of what is known of the general wave spectrum, the following conclusions may be drawn.

From (1) (no regular reflexion obtained), it is evident that the wave-length must be small, for regular reflexion effects are obtainable with polished metal, glass, quartz, etc. for radiations in sections A to F. While diffuse reflexion effects are obtained with entladungstrahlen, no

\* Millikan, using a vacuum spectrograph with a ruled grating, and a high potential vacuum spark, has observed spectral lines between .000 Å. and 136 Å. X-rays of very long wave-length lying in this region (G) have been produced by means of low velocity cathode rays and photo-electrons.

Fig. 14.





reflexion is obtained with X or  $\gamma$  rays. (The reflexion of X-rays from crystals is of course an interference effect, and not pure reflexion.) From this it is to be inferred that the radiation cannot lie in sections A, B, C, D, E, or F. This is indicated in fig. 14 by the thick line running from A to F, opposite (1), marked "diffuse reflexion."

From (2) ("ionization of air") also, it would appear that the wave-length is small, for none of the radiations in sections A, B, C, or D are known to ionize gases. Ultra-violet and Schumann's rays exhibit ionization effects, while entladungstrahlen, X-rays, and  $\gamma$ -rays are strong ionizing agents. Hence, proceeding as in the case of (1), the thin and thick parts of line (2) ("ionization of air") indicate the regions in which the radiation could or could not lie as determined by this property of ionization.

Property (3) (most substances opaque, but thin celluloid transparent) furnishes evidence of a more definite character than either of the other two. Had the radiation been of the type met with in A or B, almost any insulator would have been transparent, while metals would have been opaque. The fact that such insulators as paraffin wax, glass, ebonite, paper, etc. were opaque therefore rules out this section. Similarly, as materials such as paper, ebonite, etc. (which permit the passage of infra-red rays) cut off the radiation, it is evident that the radiation is not in the infra-red region. Had it been in section D (visible spectrum), glass etc. would have transmitted it, while the fact that quartz cuts off the effect shows that it cannot be in the ultra-violet down to a wave-length of about 2000 Å. (limit of quartz = 1850 Å.). Most substances are opaque to Schumann's rays and to entladungstrahlen, so that no definite statement can be made with regard to regions F and G. The fact, however, that a thin celluloid film is transparent to the radiation is consistent with the view that it is some type of entladungstrahlen. X-rays (sections H and K) next claim attention. With the exception of soft X-rays (long wave-length) the radiations in this region have large penetrative powers. As the radiation in question was stopped by most substances, it is evident that it could not have been any form of X-ray other than one of extremely long wave-length. This fact was further verified, for on exposing to the radiation an X-ray photographic plate wrapped in paper, and developing, it was observed that no radiation had penetrated the paper and affected the plate. The time of exposure was sufficiently long for the presence of any X-ray which could ionize the

gas in the gap to be recorded on the plate. Hence it was inferred that no such radiation (*i. e.*, one capable of penetrating the paper—say of greater wave-length than a few Ångström units) was present in such intensity as to be the cause of the ionization.

Of still shorter wave-length than the X-rays are the  $\gamma$ -rays of radioactive substances, which are the most penetrating rays known—a fact which precludes the possibility of the radiation from the discharge being in this region. Beyond this, no further type of radiation is known. It is probable, however, that if a radiation of shorter wave-length than the  $\gamma$ -rays is discovered, it will be of high penetrative power. In accordance with the method applied to (1) and (2), line (3) therefore indicates that the radiation cannot lie in sections A, B, C, D, E, nor in sections K and L.

Property (4) (penetration of air) indicates that the radiation cannot lie in sections F and H. Section F (Schumann's rays) comprises the extreme ultra-violet region, a type of radiation with general properties similar to those of ultra-violet radiations, but highly absorbed by air, especially near the low wave-length end of the region. (At a wave-length of 1000 Å. a millimetre of air at ordinary pressure will absorb the radiation almost completely.) The very long wave-length X-rays are also absorbed by air. [In carrying out investigations in these regions, vacuum spectrographs have to be used.] The thickened portions of line (4) therefore indicate that the radiation cannot lie in sections F and H.

The only range of the general wave spectrum from which the radiation under consideration is not debarred by one or more of its properties is section G (in which no thick line appears in the diagram), extending from a wave-length of approximately 1000 Å.\* to about 13 Å.—a considerable range. As has already been explained, the only radiation known and examined within this region is entladungstrahlen, and its properties and wave-length have not yet been fully determined. As the wave-lengths of entladungstrahlen have not been determined, it is impossible

\* As, in his experiments on spectral lines, Millikan used an artificial diffraction grating for measuring wave-lengths, it is reasonable to conclude that regular reflexion effects can be obtained with the wave-lengths he dealt with. Also, since a vacuum spectrograph had to be used, waves in this region must have been absorbed by air. These two facts appear to narrow the region in which the radiation concerned can lie, from 1000 Å.—13 Å. to 136 Å.—13 Å.

to state what position they occupy in the region. Further, the scanty information as to their properties rendered difficult the task of determining whether the rays emitted by the pilot discharge corresponded to some form of them, or to some other, hitherto unknown, radiation lying in this region. Another difficulty arose from the highly absorbable nature of the radiation, which rendered most of the tests applied of a negative character.

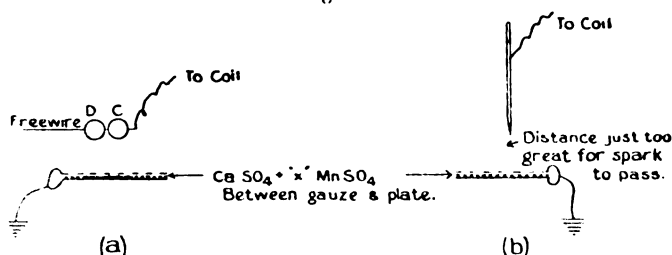
Of the six properties specified as characteristic of entladungstrahlen, it will be observed that the first four are characteristic of the radiation now considered. In addition, the fifth is characteristic when the pilot discharge is a spark. This indicated the possibility of the radiation being a form of entladungstrahlen. It remained therefore to investigate whether the sixth property of entladungstrahlen (thermoluminescence) was also a property of the radiation.

A thermoluminescent salt ( $\text{CaSO}_4 + "x" \text{MnSO}_4$ ) was prepared. Various methods of preparation were tried, but the best salt was produced when calcium sulphate was precipitated from a solution of calcium chloride by means of a solution of manganese sulphate. The precipitate was washed, dried, and heated to a high temperature for some time. As a test for sensitiveness, some of the resulting powder was placed near the main gap, so that the radiation from the main spark (which contained entladungstrahlen) fell on it. After an exposure of about half a minute, the powder was gently warmed in a dark room. A bright green glow indicated that the radiation from the main spark had excited thermoluminescence in the salt. As this phenomenon is supposed to be produced in this particular salt only by entladungstrahlen and cathode rays, it could be used as a test for the presence of entladungstrahlen when cathode rays were known to be absent.

As the "pilot gap" type of third electrode (fig. 13) (spark discharge) could affect the gap from a greater distance than could the point, it was tried first. The salt was spread in a thin layer on an earthed metal plate, an earthed gauze being placed above it (fig. 15 a). The pilot gap was then placed a few centimetres above this, and the salt exposed to the radiation from the pilot spark. It was observed that a definite glow could be obtained on heating after an exposure of half an hour. From this, it was clear that *while entladungstrahlen capable of producing thermoluminescent effects were emitted by the*

*pilot spark, they were much less intense than those emitted by the main spark.* As to this, however, it must be remembered that the pilot spark was only about half a millimetre in length, and "thin," while the main spark was about five millimetres long, and "intense." In the experiments on the properties of entladungstrahlen, the sparks used were longer than either of these \*, and it had been observed that an "intense" spark gave a stronger thermoluminescence than a "thin" one of the same length. This explains why such a long exposure was needed in the case of the pilot spark.

Fig. 15.



The "pilot gap" of the last experiment was now replaced by the third point (fig. 15 *b*), which was arranged above and as near to the gauze as possible, without allowing sparks to pass from the point to the gauze (*i. e.*, so that the discharge was "silent"). The results of about twenty tests, in which the salt was exposed to the radiation from the point for various times ranging from a quarter of an hour to four hours, showed no definite evidence of the presence of thermoluminescence. In one case only, after an exposure of seventy-five minutes a very faint glow was observed on heating the salt, but as this effect was not obtained again, even with exposures as long as four hours, it was assumed that it was caused by the entladungstrahlen emitted by the stray sparks which occasionally passed from the point to the gauze.

While the thermoluminescent effects obtained in the case of the pilot spark definitely indicate the presence of entladungstrahlen in the rays emitted by the discharge, the absence of such effects in the case of the silent discharge does not necessarily imply that no entladungstrahlen are present. In the first place, it is conceivable that entladungstrahlen might be present of intensity sufficient

\* E. Laird (Phys. Rev. 1910, i. p. 293) employed a spark of 1.5 cm.

to produce ionization effects, but not to affect the salt to such an extent as to produce visible thermoluminescent effects. The view is consistent with the observed fact that ionization effects are more readily obtained than thermoluminescent effects. It is also to be remembered that the radiation from the silent discharge was not so intense as that emitted from the spark, as the latter could penetrate a layer of air ten centimetres thick, while the former could penetrate only six centimetres.

Secondly, it is possible that the radiations emitted by spark and silent discharges while both within the same region G, may be of different wave-lengths. Ionization effects are to be expected from any radiation within this region, as most low wave-length radiations ionize gases. On the other hand, thermoluminescence is most probably a phenomenon produced only by particular wave-lengths, or ranges of wave-length. If such is the case, the absence of any thermoluminescence in the case of the silent discharge could be explained by assuming that while there is present a radiation capable of ionizing the gas in the gap, the particular radiation capable of producing thermoluminescence is absent. Similarly, in the case of the spark discharge, it could be assumed that there is present, either one radiation capable of producing both effects, or else two radiations, one producing ionization and the other thermoluminescence.

While the evidence available is not sufficient to establish either of these suggestions (which are only put forward tentatively as showing that the absence of thermoluminescence in the case of the silent discharge does not necessarily imply the absence of entladungstrahlen), it is interesting to note that different types of spark discharge give rise to entladungstrahlen of various intensities. For example, the entladungstrahlen emitted from an "intense" spark are found to be more penetrating than those emitted from a "thin" spark of equal length. A penetrating type is also emitted from the lengthened spark discharge produced at a pressure of only one or two millimetres of mercury\*, and it has been observed that entladungstrahlen are also emitted from the luminous parts of the discharge in a vacuum tube. [As far as the writer is aware, it does not seem to have been investigated whether or not they are emitted from a silent discharge at ordinary pressure.] From this it seems reasonable to expect that the conditions under which the

\* See Phys. Rev. 1909, xxviii. (Mar.) p. 225.

discharge takes place should influence the type of radiation emitted, in the sense that while radiations from all types of discharge might produce ionization, only the wave-lengths emitted from particular types could produce thermoluminescent effects. Further work on the radiation in this region would probably give interesting results in this connexion.

Summarizing the results of the experiments as a whole, it may be stated that :

(1) Before the three-point phenomenon can be obtained, some form of discharge, silent or spark, must be "visible" from the main gap, and within a certain distance of it.

(2) The phenomenon is obtained in the absence of

(a) disturbances of the electric field near the main gap, and

(b) the passage of ions from the pilot discharge into the main gap.

(3) A radiation is emitted by the pilot discharge, which can ionize the gas in the main gap.

(4) When this radiation is prevented from reaching the main gap, the usual three-point effect is not obtained.

(5) The three-point effect is still produced when the electrodes are so shielded as to prevent any photo-electric effects being ~~shunted~~ by the radiation.

(6) The observed properties of this radiation seem to establish the limits of its wave-length as being approximately 1000 Å. and 13 Å., and they coincide to a large extent with the corresponding properties of entladungstrahlen.

*It is therefore inferred that the three-point effect is caused by the ionization of the gas in the main gap by a radiation, believed to be a form of entladungstrahlen, emitted by the pilot discharge. Disturbances of the field, passage of ions into the gap, or photo-electric effects produced by the radiation or by ultra-violet light, while possibly assisting in, are not essential for, the production of the three-point effect. (It is interesting to note that when the radiation is prevented from reaching the gap by means of a quartz plate, photo-electric effects at the electrodes due to ultra-violet light emitted from an intense pilot discharge and transmitted by the plate, may give rise to a diminished form of three point effect. Under these conditions, of course, the ultra-violet light is the main cause of the effect.)*

If the radiation proves to be a form of entladungstrahlen, two interesting facts are disclosed regarding it.

(1) That entladungstrahlen are produced in air at ordinary pressure by a silent discharge as well as by a spark.

(2) That a critically adjusted spark gap subjected to impulsive voltages forms a convenient indicator of the presence of entladungstrahlen (when no other radiations are present which ionize gases or produce photo-electric effects), and that it appears to be more sensitive in use than either an ionization chamber or a thermoluminescent salt.

Incidentally, it is suggested that possibly either or both of the modified types of three-point gap used in this work might, on investigation, prove to be more suitable as a standard type of gap than the usual type employed, in which an insulated pointed third electrode is used.

In conclusion, the writer desires to thank Dr. Taylor Jones for the interest he took in the work and the suggestions he made during the progress of it. The experimental part of the work was carried out in the Physical Laboratory of the University College of North Wales, Bangor.

XXIX. *On the best Linear Relation connecting Three Variables.* By F. J. W. WHIPPLE\*.

1. **T**HE choice of the best linear relations connecting any number of variables was the subject of a paper published† in the 'Philosophical Magazine' by Professor Karl Pearson in 1901. Approaching the question from a geometrical standpoint, Pearson gave his paper the title "The Lines and Plans of closest Fit to Systems of Points in Space." A "supplementary" paper was published recently‡ by Professor H. S. Uhler, "Determination of the Minimum Plane in Four-Dimensional Space with respect to a System of Non-Coplanar Points." This was followed§ in the next issue of the 'Philosophical Magazine' by a paper by Mr. H. Glauert, "The Determination of the best Linear Relationship connecting any Number of Variables." This last communication appears to have been written without knowledge of Pearson's work.

In all these three papers the criterion by which best fit is defined is the same. The plane or line of best fit is such that the sum of the squares of the perpendiculars from the

\* Communicated by the Author.

† Phil. Mag. (6) ii. p. 559 (1901).

‡ Phil. Mag. (6) xlix. p. 1260 (June 1925).

§ Phil. Mag. (6) l. p. 250 (July 1925).

points in question on to that plane or line is a minimum. Now, when other variables are represented by the coordinates of points, the question of scale assumes great importance. If the scale on which one variable is represented is doubled, so that one coordinate (say,  $x$ ) of each of the representative points is doubled, the new plane of closest fit will not be related in any simple way to the old one. In so far as Professor Uhler deals with the geometrical representation of statistics, he says that his variables "are treated as having equal mathematical weights." Mr. Glauret is more explicit. He makes the assumption that the variables involved in the analysis fall into two classes, one subject to errors of observation and the other known accurately. He assumes that if there had been no errors of observation the variables would have satisfied exactly an equation of the first degree. Moreover, he assumes that, for each of the variables which are subject to errors of observation, the probable magnitude of an error is the same.

In most statistical problems these assumptions could not be justified. There is no *a priori* reason to anticipate that the variables satisfy an equation of the first degree exactly. What we wish to obtain is an equation of the first degree which is the best available as an indication of the type of interdependence of the variables. Glauret's second assumption is really an instruction \* to choose the units for the several variables so that the probable errors will have the same numerical value. There is no general method available for the selection of such units. To select units so as to give the "standard deviations" of the variables from their mean values the same numerical value is a device well known to meteorologists through the work of Mr. W. H. Dines; it does not meet Mr. Glauret's requirements, but it has the advantage of making the choice of units depend on the nature of the variations under investigation rather than on such an accident as the accuracy with which they can be measured. For example, two investigators may be dealing with a problem in which temperature has to be measured over a range of  $50^{\circ}\text{C}$ . One investigator considers that his temperatures have a probable error of  $1^{\circ}\text{C}$ ., the other claims that his probable error is  $0^{\circ}\cdot 1\text{C}$ . With Glauret's criterion the results of the two observers should be plotted on different scales, and the linear relations arrived at when temperature

\* That this is also Prof. Uhler's meaning can be seen by reference to his paper, "Method of Least Squares and Curve Fitting," Journal of the Optical Society of America and Review of Scientific Instruments, vol. vii. no. 11, p. 1043 (1923).



is correlated with other variables will be quite different. With Dines's criterion the scales will be the same and the results the same for the two observers.

2. As has been mentioned, the problem which presents itself in statistical inquiries is to obtain the equation of the first degree which is the best available as an approximate relation between the variables. To define more precisely what is meant by "best" in this connexion we must use symbols. To simplify matters we consider only \* the case of three variables.

Let  $x_1, x_2, x_3$  be the departures of the three variables from their mean values.

Let  $a, b, c$ , be three undetermined coefficients, and let

$$ax_1 + bx_2 + cx_3 = \epsilon. \quad . \quad . \quad . \quad (1)$$

If the variables  $x_1, x_2, x_3$  had been uncorrelated, then each of the expressions

$$\Sigma x_2 x_3, \Sigma x_1 x_3, \Sigma x_1 x_2$$

would have been zero (the summation denoted by  $\Sigma$  extending over all the observed values of  $x_1, x_2$ , and  $x_3$ ). In that case  $\Sigma \epsilon^2$  would have been equal to

$$a^2 \Sigma x_1^2 + b^2 \Sigma x_2^2 + c^2 \Sigma x_3^2.$$

It is reasonable to say that the equation,

$$ax_1 + bx_2 + cx_3 = \epsilon,$$

is the best available representation of the relation between the variables, if  $a, b, c$  are so chosen that  $\Sigma \epsilon^2$  bears as small a ratio as possible to

$$a^2 \Sigma x_1^2 + b^2 \Sigma x_2^2 + c^2 \Sigma x_3^2.$$

This definition has the advantage that it is independent of the units in terms of which the variables are measured. If  $x_1, x_2, x_3$  are multiplied by constant factors, then the best fitting linear relation is determined consistently by the straightforward algebraic transformation.

3. Let us write

$$\lambda = \frac{\Sigma (ax_1 + bx_2 + cx_3)^2}{a^2 \Sigma x_1^2 + b^2 \Sigma x_2^2 + c^2 \Sigma x_3^2}. \quad . \quad . \quad . \quad (2)$$

\* The somewhat trivial case of two variables is dealt with below, p. 384.

Since  $\lambda$  is to be a minimum for variations of  $a$ , it follows that

$$\lambda a \Sigma x_1^2 = a \Sigma x_1^2 + b \Sigma x_1 x_2 + c \Sigma x_1 x_3. \quad (3)$$

If the number of "observations" is  $n$ , the standard deviations  $\sigma$  and the correlation coefficients  $r$  are defined by equations such as

$$n\sigma_1^2 = \Sigma x_1^2, \quad (4)$$

$$nr_{12}\sigma_1\sigma_2 = \Sigma x_1x_2. \quad (5)$$

Accordingly, equation (3) may be written

$$\lambda a\sigma_1 = a\sigma_1 + br_{12}\sigma_2 + cr_{13}\sigma_3. \quad (6)$$

In the same way the conditions for  $\lambda$  to be a minimum for variations of  $b$  and  $c$  may be written down, so that we have the three equations

$$\left. \begin{aligned} (1-\lambda)a\sigma_1 + r_{12}b\sigma_2 + r_{13}c\sigma_3 &= 0, \\ r_{12}a\sigma_1 + (1-\lambda)b\sigma_2 + r_{23}c\sigma_3 &= 0, \\ r_{13}a\sigma_1 + r_{23}b\sigma_2 + (1-\lambda)c\sigma_3 &= 0. \end{aligned} \right\} \quad (7)$$

By elimination of  $a, b, c$ , we find that

$$\begin{vmatrix} 1-\lambda & r_{12} & r_{13} \\ r_{12} & 1-\lambda & r_{23} \\ r_{13} & r_{23} & 1-\lambda \end{vmatrix} = 0. \quad (8)$$

The parameter  $\lambda$  is the least positive root of this equation. When  $\lambda$  has been determined the ratios of the coefficients  $a, b, c$  are given by the equations of the preceding group.

4. Since the condition  $\lambda=1$  would indicate complete independence of the variables, whilst the condition  $\lambda=0$  would indicate that they satisfied exactly an equation of the first degree, it is appropriate to call  $1-\lambda$  the coefficient of mutual correlation and to denote it by a symbol  $R_{123}$ . When there is no risk of confusion the suffixes may be omitted.

It will be seen that the coefficient of mutual correlation is the greatest root of the equation,

$$\begin{vmatrix} R & r_{12} & r_{13} \\ r_{12} & R & r_{23} \\ r_{13} & r_{23} & R \end{vmatrix} = 0. \quad (9)$$

When  $a, b, c$  have the values given by (7) the equation

$$ax_1 + bx_2 + cx_3 = \epsilon \quad . \quad . \quad . \quad (10)$$

may be called the mutual regression equation. It can be written

$$\begin{vmatrix} x_1/\sigma_1 & x_2/\sigma_2 & x_3/\sigma_3 \\ r_{12} & R_{123} & r_{23} \\ r_{13} & r_{23} & R_{133} \end{vmatrix} = \epsilon \quad . \quad . \quad (11)$$

An alternative form is

$$\frac{x_1}{\sigma_1}(R_{123}^2 - r_{23}^2)^{\frac{1}{2}} \pm \frac{x_2}{\sigma_2}(R_{123}^2 - r_{13}^2)^{\frac{1}{2}} \pm \frac{x_3}{\sigma_3}(R_{123}^2 - r_{12}^2)^{\frac{1}{2}} = \epsilon. \quad (12)$$

This form is more symmetrical, but it suffers from the drawback that the signs to be attributed to the radicals have to be determined by comparison with equations such as (11).

The criterion adopted—namely, that  $\Sigma \epsilon^2$  should bear as small a ratio as possible to  $a^2 \Sigma x_1^2 + b^2 \Sigma x_2^2 + c^2 \Sigma x_3^2$ —has led to the same linear equation as would have been arrived at by regarding the variables as coordinates, plotted on such scales that each of the three standard deviations was represented by the unit of length, and finding the plane of closest fit.

5. In equations (10) and (11) the right-hand side is written as  $\epsilon$ , not as zero. This is an indication that the variables do not satisfy exactly the equations which would result from the substitution of 0 for  $\epsilon$ . It is useful, however, to have the equations written in such a way that the magnitude of the departure from zero is indicated. This can be done by introducing\* the symbol  $\text{Ca}$  to signify a "casual" number, the standard value of which, i. e., the square root of the mean value of the square, is unity.

In this way we can write (10) in the form

$$\frac{ax_1 + bx_2 + cx_3}{(a^2\sigma_1^2 + b^2\sigma_2^2 + c^2\sigma_3^2)^{\frac{1}{2}}} = (1-R)^{\frac{1}{2}} \text{Ca}. \quad . \quad . \quad (13)$$

Similarly, in place of (12) we have the equation

$$\frac{\frac{x_1}{\sigma_1}(R^2 - r_{23}^2)^{\frac{1}{2}} \pm \frac{x_2}{\sigma_2}(R^2 - r_{13}^2)^{\frac{1}{2}} \pm \frac{x_3}{\sigma_3}(R^2 - r_{12}^2)^{\frac{1}{2}}}{(3R^2 - r_{23}^2 - r_{13}^2 - r_{12}^2)^{\frac{1}{2}}} = (1-R)^{\frac{1}{2}} \text{Ca}. \quad . \quad (14)$$

It will be noticed that in the very special case in which

\* 'Royal Meteorological Society, Quarterly Journal,' l. p. 237 (1924).

$R_{123}$  is unity, the three ordinary regression equations, such as

$$\begin{vmatrix} x_1/\sigma_1 & r_{12} & r_{13} \\ x_2/\sigma_2 & 1 & r_{23} \\ x_3/\sigma_3 & r_{32} & 1 \end{vmatrix} = (1-r_{23}^2)^{\frac{1}{2}} \begin{vmatrix} 1 & r_{12} & r_{13} \\ r_{12} & 1 & r_{23} \\ r_{13} & r_{23} & 1 \end{vmatrix} \text{Ca}$$

are all equivalent to each other and to the mutual regression equation,

The casual number, or residual, determined by equation (14), is correlated, of course, with  $x_1$ ,  $x_2$ , and  $x_3$ . If  $r_{1.123}$  is the correlation coefficient for the residual and  $x$ , then

$$r_{1.123}^2 = \frac{(1-R)(R^2-r_{23}^2)}{3R^2-r_{23}^2-r_{13}^2-r_{12}^2}, \quad \dots \quad (15)$$

and it follows that

$$r_{1.123}^2 + r_{2.123}^2 + r_{3.123}^2 = 1 - R. \quad \dots \quad (16)$$

6. The special cases, in which two of the three correlation coefficients  $r_{12}$ ,  $r_{13}$ ,  $r_{23}$  are equal, are of interest.

If  $r_{12}=r_{13}<r_{23}$  and  $r_{23}$  is positive, then the greatest root of the equation in  $R$

$$\begin{vmatrix} R & r_{12} & r_{13} \\ r_{12} & R & r_{23} \\ r_{13} & r_{23} & R \end{vmatrix} = 0$$

is equal to  $r_{23}$ . In this case the mutual regression equation (14) reduces to

$$\frac{1}{\sqrt{2}} \left[ \frac{x_2}{\sigma_2} - \frac{x_3}{\sigma_3} \right] = (1-r_{23})^{\frac{1}{2}} \text{Ca}. \quad \dots \quad (17)$$

and does not contain  $x_1$  at all.

On the other hand, if  $r_{12}=r_{13}>r_{23}$  and  $r_{23}$  is positive, then  $r_{23}$  is the smallest root of the critical equation instead of the largest.

The equation reduces to

$$(R-r_{23})(R^2+r_{23}R-2r_{12}^2)=0, \quad \dots \quad (18)$$

and the greatest root is given by

$$R = \frac{1}{2} [(r_{23}^2 + 8r_{12}^2)^{\frac{1}{2}} - r_{23}]. \quad \dots \quad (19)$$

Finally, if  $r_{23}$  is negative and  $r_{12}=r_{13}$ , then (19) gives the only positive root of the critical equation.

In either of these last two cases the mutual regression

equation is of the symmetrical form

$$a \cdot \frac{x}{\sigma_1} - \frac{y}{\sigma_2} - \frac{z}{\sigma_3} = \epsilon, \quad . \quad . \quad . \quad . \quad (20)$$

with 
$$a = \frac{r_{12}(R - r_{23})}{r_{12}^2 - r_{23}R}.$$

The three cases in which  $r_{12} = -r_{13}$  can be dealt with in the same way.

7. It is a question of practical importance whether the mutual regression equation represents a real addition to knowledge. It will do so if the mutual correlation coefficient is considerably greater than any of the correlation coefficients for the pairs of variables. In the extreme case in which  $R$  is unity the three coefficients are related like the cosines of three angles whose sum is  $360^\circ$ . For instance, with  $r_{12} = r_{13} = r_{23} = -\frac{1}{2}$ , the mutual regression coefficient is unity and the mutual regression equation may be written

$$\frac{x_1}{\sigma_1} + \frac{x_2}{\sigma_2} + \frac{x_3}{\sigma_3} = 0 \text{ Ca.}$$

In general, for  $R$  to be much greater than the numerical value of any of the three  $r$ 's, the product of these three must be negative.

When the three variables  $x_1, x_2, x_3$  are regarded as co-ordinates of points in three-dimensional space we can entertain the possibilities that the points may have a spindle-like distribution or a disk-like distribution. In the former case a straight line is a good approximate representation, in the latter a plane. Such a plane is defined by the mutual regression equation. The range of utility of mutual regression equations is indicated by the geometrical illustration.

#### 8. *Note on the Correlation of Two Variables.*

With two variables the mutual correlation coefficient is numerically equal to the ordinary correlation coefficient, as may be seen from the fact that in the case of two variables the analogue of equation (9) is  $R^2 - r_{12}^2 = 0$ . The mutual regression equation for two variables is

$$\frac{1}{\sqrt{2}} \left( \frac{x_1}{\sigma_1} \mp \frac{x_2}{\sigma_2} \right) = (1 \mp r_{12})^{\frac{1}{2}} \text{ Ca,}$$

the upper sign of the ambiguities being taken if  $r_{12}$  is positive, the lower if it is negative.

XXX. *On the Separation of Crystalloids from one another by Dialysis.* By LOUIS KAHLENBERG, Ph.D., Professor of Chemistry, University of Wisconsin\*.

*Introduction.*

ON the basis of the data which Thomas Graham† collected in his classical experiments on osmosis and dialysis, he classified substances into crystalloids and colloids. The crystalloids were crystalline bodies which he had found passed through animal bladder or parchment. On the other hand, non-crystalline or glue-like bodies he found did not go through the membranes he employed, and to these bodies he gave the name colloids. Ever since Graham's time it has been held that crystalline substances go through membranes, and non-crystalline substances (*i. e.* colloids) do not. While Graham's experiments were fundamental and important, the data which he collected at that early time were limited in number. Moreover, he used relatively few solutions and tested them with but few membranes, so that, while his deductions were quite in harmony with his experimental observations, the latter were far too limited in number to afford a sufficiently broad basis of induction for such general conclusions as he drew, and as have been held by scientists and expounded in text-books during all of the decades since Graham's time.

The fact is that crystalline substances can very well be separated from one another by dialysis. All that is necessary is to select suitable membranes and solutions to accomplish this. Indeed, it is even quite possible to separate "crystalloids" from "colloids" by having the "*colloids*" pass through the membrane and the "*crystalloids*" remain behind, if the proper septum and the proper solvent be employed. To complete the statement of the situation, one can also separate "colloids" from "colloids" by dialysis, by choosing the proper solvent and membrane. In my experimental researches "*On the nature of the process of Osmosis and Osmotic Pressure with observations concerning Dialysis*"‡, specific examples of each of these cases are given.

\* Communicated by the Author.

† Philosophical Transactions, cli. part 1, p. 183 (1861); also Phil. Mag. (4) xxiii. p. 204 (1862).

‡ 'Journal of Physical Chemistry,' x. pp. 144-209 (1906); also Trans. Wis. Acad. Sci., Arts, & Letters, xiv. part 1.

The purpose of the present investigation is to present additional cases of separation of crystalloids from one another by dialysis in non-aqueous solutions, and to show that such separations can also be accomplished in aqueous solutions. Up to the present time, the separation of crystalloids from one another by dialysis in aqueous solutions has offered peculiar experimental difficulties. Indeed, such separations have commonly been regarded as impossible, though it is well known to physiologists that processes of this kind actually take place continually in plants and animals as they live. It was the experimental study of dialysis in non-aqueous solutions that suggested the line of attack to obtain similar results with aqueous solutions.

#### EXPERIMENTAL.

##### (a) *Non-aqueous Solutions.*

In the dialysis of non-aqueous solutions a rubber membrane, vulcanized caoutchouc, was employed. This membrane was of the sheet-rubber or so-called rubber-dam material commonly used by dentists. It was found to be fairly uniform and pliable. It could readily be stretched over the mouth of a thistle tube and secured perfectly by means of windings of stout cotton thread. The area of the membrane obtained by thus tying the sheet-rubber over the mouth of the thistle tube was about 5 sq. cm., while the capacity of the bell of the thistle tube was 50 c.c. Twenty-five cubic centimetres of the solution to be dialysed were placed in the tube so prepared, and the latter was then immersed in the pure solvent so that the level of the liquid in the outer dish was about the same as that in the tube.

After testing the action of a large number of liquids on rubber, it was found that pyridine was by far the most suitable one for the dialysis experiments. Water, of course, could not be used, for, not being absorbed by rubber, no osmotic action occurred. Alcohol, being but slightly absorbed by rubber, gave a little action, but it was entirely too slow. Hydrocarbons and their halogen substitution products did very well, but they soon softened the rubber so greatly that the membrane became distended, smeary, and too weak. Esters, ketones, aldehydes, and nitriles also proved to be unsuitable, acting too slowly or exerting too great a solvent action and consequently disintegrating the

rubber. On the other hand, pyridine is readily imbibed by rubber without appreciably weakening, disintegrating, or even unduly distending the rubber membrane. Indeed, sheet-rubber soaked by pyridine may be freed from the latter by wringing the liquid out as one would wring water from a cloth. The rubber when then hung out on a line will "dry" much the same as will a cloth that has been wet with water.

Pyridine will dissolve a great variety of substances. One would naturally expect this, for it is miscible in all proportions with water on the one hand, and also with practically all organic solvents on the other hand. Thus many substances dissolve in pyridine which are also soluble in hydrocarbons. Such substances invariably pass through rubber membranes in dialysis experiments,\* for rubber itself is practically a hydrocarbon in nature. On the other hand, pyridine also dissolves certain substances that are soluble in water but not soluble in hydrocarbons; and such substances do *not* pass through rubber membranes. So, for example, sulphur, naphthalene, and camphor dissolve in pyridine. They are also soluble in hydrocarbons, therefore in rubber, and they consequently all pass through rubber membranes upon dialysis. Again, silver nitrate, lithium chloride, and cane-sugar are soluble in pyridine but not in hydrocarbons, therefore not in rubber, and consequently they do not pass through rubber membranes. From these facts one would conclude that the following substances may be separated from each other by dialysis in pyridine solutions using rubber membranes, the substance first named in the case of each pair passing through the membrane:—Sulphur from sugar; naphthalene from sugar; sulphur from silver nitrate; naphthalene from silver nitrate; camphor from sugar; camphor from silver nitrate; sulphur from lithium chloride; camphor from lithium chloride; naphthalene from lithium chloride. It was actually found in the laboratory that these separations can be made by means of dialysis as above described. The solutions used contained 1·5 per cent. of each of the substances in question. The dialysis proceeded quite normally, the length of time required to secure practically complete separation varying from two days to three weeks. When rather thin membranes were used and the outer liquid was renewed every two or three hours, the time required to effect the separation was materially shortened.

\* Compare Kahlenberg, *Journ. Phys. Chem.* x. p. 141 (1906).



(b) *Aqueous Solutions.*

Among the precipitated membranes, first devised by Moritz Traube\* and employed by Pfeffer† in his osmotic investigations, the copper ferrocyanide membrane was perhaps the most successful one. It is well known that this membrane is practically impervious to sugar. On the other hand, quite a number of other substances will pass through this septum. Urea, for instance, will pass through fairly readily. It ought, therefore, to be possible to separate sugar from urea by means of a copper ferrocyanide membrane. Such was actually found to be the case. A copper ferrocyanide membrane was formed in a good quality of thin parchment paper that was tied over the mouth of a tube by means of stout thread. Great care had to be exercised in securing the membrane properly, and indeed it was only after a number of trials that a membrane free from leaks was finally obtained. The copper ferrocyanide precipitate was formed in the membrane in the usual way; namely, by first soaking the parchment in water so as to eliminate air-pockets, and then placing a 5-per-cent. solution of copper sulphate on one side of the paper and a solution of potassium ferrocyanide of about the same concentration on the other. After several hours' standing these solutions were removed, the membrane well rinsed with water, and the dialysis begun.

The solution in the dialyser contained 2 grams of sucrose and 2 grams of urea in 100 c.c. The outer liquid was pure water. The area of the membrane was about 100 sq. cm. For a period of five days urea only passed out of the dialyser, showing that sugar and urea were actually being separated from each other by dialysis. The outer liquid was continually renewed in an effort to remove all of the urea from the solution. Thus far it has not been possible to accomplish this without some of the sugar also passing through the membrane after five to ten days. In other words, the membrane became defective after that time. The fact that such membranes are apt to become leaky after being in use for a time has also been observed by others. During these experiments it was found that not only sucrose, but also maltose, lactose, galactose, dextrose, and lævulose do not pass through copper ferrocyanide membranes. The observations were confirmed with four different and quite perfect membranes. Urea, on the other

\* *Archiv. für Anat. u. Physiol.* p. 87 (1867).† *Osmotische Untersuchungen*, Leipzig (1877).

hand passed through all of these membranes. My thanks are due to Mr. H. D. Baernstein for help in carrying out the experiments with the copper ferrocyanide membranes.

Lanoline, the fat of the wool of the sheep, is known to be able to absorb more than 50 per cent. of its weight of water. It occurred to me that this hydrated lanoline would probably exhibit selective osmotic properties, and such, indeed, proved to be the case. A very large amount of time and labour had to be expended in finding a satisfactory method of preparing osmotic membranes of lanoline. In this work my assistant, Dr. John R. Koch, and my son, Dr. Herman H. Kahlenberg, were especially helpful in the laboratory. With their aid and enthusiasm it was possible to carry out a very large number of experiments that finally yielded good results.

In order to produce osmotic membranes of lanoline, the latter had to be absorbed in suitable inert supporting material. As such materials, fine muslin, linen, silk, copper gauze, and parchment paper were tried. These materials were tied over the mouth of a tube and then soaked in molten lanoline, care being taken in this process to get rid of occluded air. The difficulty arose in getting perfectly uniform and sufficiently thin membranes that were quite free from flaws. If the membranes were too thick, their action was slow; on the other hand, the effort to secure thin membranes naturally frequently resulted in getting defective ones. After many trials, it was found that a fine quality of China silk and a good, rather thin, parchment paper were the best materials in which to absorb the lanoline to obtain good working membranes. In tying the material over the mouth of a tube, silk was, of course, much better than parchment, for the stiffness of the latter made it more difficult to secure it to the glass without leaks. On the other hand, when parchment bags were used, this difficulty was obviated, and excellent, quite thin membranes were obtained. In the present research, membranes of silk impregnated with lanoline were used. After carefully tying the silk over the mouth of the thistle tube, the silk was dipped in molten lanoline and moved about in the latter so as to get rid of air-bubbles. The tube was then removed from the lanoline bath and held near a flame so that the excess of lanoline ran off. In this process the tube should be slowly rotated and manipulated so as to secure as even a distribution of the lanoline in the silk as possible. By careful manipulation and repeated dipping of the membrane, if necessary, satisfactory, continuous films of lanoline in the

silk fabric may be obtained. Gross leaks in such membranes could be detected by simply filling the tube with water and suspending it in the air for a while, when the water would drip from the membrane if the latter was very defective. However, the absence of such dripping was by no means proof that the membrane was sufficiently tight for osmotic experiments. By filling the tube with Congo red solution and immersing it in water, it was found that the membrane was generally tight if none of the dyestuff appeared in the outer liquid. However, this test also was not absolutely reliable, for if any salts were dissolved in the water to which the Congo red had been added, the latter was frequently precipitated, and consequently did not make its way through the membrane in spite of the fact that it was not absolutely free from leaks. A solution of cane sugar, or one of nickel chloride, was found best as a means of testing the membranes. If these solutions did not pass through, the membrane was quite tight.

It should be remarked here that, besides preparing lanoline membranes by imbibing that fat in materials like silk, parchment, etc., as stated above, the attempt was made to impregnate collodion membranes with lanoline, or to deposit a film of the latter on the inner side of a collodion sack. The attempts to dissolve lanoline in collodion or to add the former to collodion solutions by first dissolving the lanoline in a solvent like ether, alcohol, carbon disulphide, acetone, petroleum ether, carbon tetrachloride, various esters, etc., and then adding this solution to the collodion, practically always failed to give satisfactory films. The membranes were either entirely too weak, or it was not possible to peel them from the glass tube or other vessel in which they had been formed. Attempts to form the sacks in porcelain or metallic dishes yielded no better results. A large amount of time was spent in efforts to secure a good osmotic membrane by this means, and in the course of this work many substances were tried. It was found that on the whole the best membranes were obtained when the lanoline was dissolved in chloroform and then added to the collodion, or when the collodion sack was first formed in the test tube or other glass vessel in the usual way, and then, just before peeling the sack out, a chloroform solution of lanoline was poured in so as to completely fill the sack and then carefully poured out again. In this way a film of lanoline was deposited on the inner side of the collodion sack which could be removed from the glass tube as usual after the smell of chloroform had

practically disappeared. Solvents other than chloroform yielded films that were not continuous, thus resulting in leaky membranes. The amount of time and care that had to be spent in thus securing perfect membranes by depositing a lanoline film on collodion was so great, and the advantage of these membranes over those obtained by soaking silk or parchment in lanoline was so small, that the collodion-lanoline membranes were not used in the final tests. On the other hand, however, it was found that by dipping silk or parchment in chloroform solutions of lanoline, very good and quite thin membranes were obtained, and such membranes were actually used with good success in this laboratory. The solution used in forming the membranes was prepared by dissolving 100 grams of lanoline in 250 c.c. of chloroform. The attempts to substitute other solvents for chloroform resulted in membranes that were leaky, weak, or otherwise poorer in quality for osmotic experiments.

Thistle tubes, over the mouth of which silk impregnated with lanoline was secured as already described, were used in the following experiments. The bell of each thistle tube had a capacity of about 50 c.c. In each case 25 c.c. of the solution to be tested was carefully poured in by means of a capillary funnel tube, and the thistle tube so charged was immersed in a small beaker in 130 c.c. of water, the water in and outside of the dialyser being arranged so as to be on the same level. A large number of dialysers were prepared. In fact, during the progress of the experiments frequently between seventy and one hundred dialysers were in operation at one time. In each case the results obtained were carefully checked by duplicate or triplicate experiments to make sure that the observations were not due to faulty septa.

Five-per-cent. solutions of each of the following substances were placed separately in dialysers as described: boric acid, borax, sodium chloride, sodium sulphate, Rochelle salt, magnesium sulphate, urea, cane-sugar, dextrose, lactose, egg albumin, litmus, fuchsine. Of these substances, urea, sodium chloride, boric acid, and borax passed through the lanoline membranes fastest. In three days quite appreciable amounts were found in the respective outer liquids. In an equal time, mere traces of sodium sulphate and magnesium sulphate had passed through their respective dialysers. Cane-sugar, lactose, and dextrose did not pass through at all, not even after two weeks. During the latter period of time only traces of Rochelle salt had passed through. Egg

albumin did not pass through, and traces of litmus appeared in the outer liquid only after eight days. No fuchsin was present in the outer liquid till after ten days, while after three weeks only 0.04 per cent. of the total fuchsin has passed out of the dialyser as determined colorimetrically. These results were corroborated by means of similar lanoline membranes prepared by dipping the silk in a solution of lanoline in chloroform. With the latter membranes it further was found that of the various acids tested, boric acid passed through fastest\*. In two days large quantities of boric acid had passed through the septum, whereas it required seven days for hydrochloric acid to pass through perceptibly. Acetic and sulphuric acids were still slower than hydrochloric acid. Citric and tannic acids passed in mere traces after 25 days, and oxalic acid did not pass through, even after 45 days.

Borax † passed through fairly rapidly, but not as fast as boric acid. In three days common salt came through in abundance. Potassium chloride and potassium iodide also passed through fairly rapidly as compared with other salts. However, Rochelle salt, sodium sulphate, potassium nitrate, and copper sulphate appeared in the outer liquid only in small quantities, even after ten days. Nickel chloride, sodium acetate, silver nitrate, magnesium sulphate, lithium chloride, ferric chloride, and potassium alum did not pass through, even after six weeks. Again, leucine, cystine, egg albumin, amino butyric acid, phenyl alanine, tyrosine, alanine, glutamic acid hydrochloride, lactose, dextrose, sucrose, mannose, galactose, fructose, and formic aldehyde did not pass through, even after six weeks of continued dialysis. Substances of a pronouncedly alkaline character attacked the membrane strongly, causing leaks, and then, of course, went through the passage formed. This was true of sodium carbonate, potassium carbonate, potassium cyanide, sodium cyanide, sodium silicate, and soap. Even 1-per-cent. solutions of these went through rapidly because of the disintegration which they had caused. Potassium permanganate in 5-per-cent. solutions decomposed the membrane in a few hours. A 1-per-cent. solution did not pass through in six weeks; but this was doubtless because the permanganate was reduced, forming

\* It is remarkable that boric acid has also been found to pass through the living human skin. Compare Kahlenberg, *Journ. Biological Chem.* lxii. p. 169 (1924).

† Borax does not pass through the living skin. See Kahlenberg, *loc. cit.*

insoluble manganese hydroxide. Potassium nitrate and potassium chlorate passed through slightly in two weeks, potassium chromate in four days, while potassium bichromate did not pass, even after four weeks. Of all of the organic compounds tested, *urea passed through the membrane most rapidly*. Only slight traces of ethyl alcohol passed through after six weeks, glycerin required ten days to make its appearance in the outer liquid, while methylene blue did not go through the membrane at all.

The facts above presented suggest the possibility of making a large number of separations of crystalloids from each other by dialysis. It has been found that such separations are not always easy to make, especially if it is desired to make complete separations; for in some cases the presence of an additional substance in solution influences the permeability of the membrane for the substances concerned. A number of separations have been made completely, and the following may be reported at this time:—

Urea from mannose. The urea passed through and was removed completely. The mannose did not appear till after 31 days, when the membrane became slightly defective. The solution contained 5 per cent. of each substance to begin with. The lanoline was absorbed in silk in this experiment.

Sodium chloride was separated from nickel chloride. The experiment lasted seven days; 5 per cent. of each salt was present in the solution when dialysis was started. In this case lanoline was absorbed in thin parchment paper.

Similarly, urea was separated from sodium chloride, the former passing through so much more rapidly that the separation was practically complete in four days.

Boric acid was separated from sucrose by dialysis. In this case, too, parchment paper was used as a backing for the membrane. The experiment lasted five days.

The separations took considerable time, for the membranes acted slowly, it having been necessary to make them sufficiently thick so that they would not develop flaws during the process of dialysis.

What is there in lanoline that gives it these wonderful, selective osmotic properties? This question naturally presents itself. Lanoline is distinguished from other fats particularly by the fact that it is very rich in cholesterine.

It was therefore indicated that cholesterine was probably the active selective ingredient. This actually proved to be the case, as was definitely demonstrated by experiments

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that were carried out in collaboration with my son, Dr. Herman H. Kahlenberg. The details of these investigations will soon be ready for publication. It should be stated here, however, that not only does cholesterol possess these selective osmotic properties, but phytosterine, the analogous non-saponifiable ingredient of plant oils, also shows practically the same properties. Since cholesterol is present in all living animal cells, it would seem likely that *it is extremely delicate films of these sterenes that give living cells their wonderfully selective osmotic properties.* Moreover, since animal oils contain cholesterol and all plant oils similarly contain phytosterine, one would naturally expect membranes made of such oils to exhibit selective osmotic properties to some degree, especially when relatively considerable amounts of these sterenes are present. This, too, has been found to be the case\*. In working out the latter fact Mr. Clarence Hrubesky, one of my assistants, has been very helpful. In preparing large quantities of pure cholesterol a number of my students have helped in the laboratory. The result has been that not only have osmotic membranes been made of these sterenes, but the latter have been carefully studied as to their physical and chemical properties. Finally, in the further separation of crystalloids by dialysis with sterene membranes, my assistant, Dr. John R. Koch, acted as collaborator in the experimental work. The results of these further researches will soon be ready for publication.

Madison, Wisconsin.

October 1925.

\* Attempts have been made to prepare osmotic membranes from materials other than lanoline or sterenes by means of the methods above described. Beeswax was tried, but was found to be perfectly inactive and impervious to all aqueous solutions as long as the septum was intact. It was found that camphor, borneol, alpha-naphthalene or beta-naphthalene, when dissolved in the various solvents mentioned above, yielded no continuous films that could be used in osmotic experiments. Furthermore, when each of these substances was dissolved in molten beeswax, lanoline, or tallow and then the resulting mass dissolved in chloroform, carbon tetrachloride, ether, ether plus alcohol, petroleum ether, or carbon bisulphide, no continuous films could be produced except when lanoline was used. The presence of the latter in any membrane always resulted in osmotic action.

XXXI. *The Air-Bubble Viscometer.**By* GUY BARR, *B.A., D.Sc.* \*

[Plate VI.]

## SUMMARY.

(a) It was desired to find whether, and under what circumstances, the rise of a large bubble in a vertical tube containing liquid could be used as an indication of the viscosity of the liquid.

(b) The effects of length of bubble and diameter of tube have been examined and the rate of rise determined for several oils of known viscosity and surface tension, for water and for glycerin in different tubes. A dimensional analysis of the problem has been made involving certain assumptions which seem to be capable of verification, in any particular case, from the appearance of the bubble.

(c) Above a certain limit the length of the bubble is without appreciable effect on the rate of rise. For bubbles rising "slowly" in a given tube, *i.e.* at such a rate that not more than one thickened annulus of liquid appears between the bubble and the walls towards the rear end of the bubble, it has been found that the rate of rise is inversely proportional to the kinematic viscosity, provided that the surface tension is constant. An approximate determination has been made of the form of the function of  $r/a$  upon which, in addition to the viscosity, the rate of rise depends. In certain conditions, *e.g.* when light oils are examined in a tube of such a diameter as to give a convenient rate of rise, the rate may vary about fourteen times as fast as the diameter and six times as fast as the surface tension, but these effects become very much less pronounced when viscous liquids are used in wide tubes.

(d) The air-bubble viscometer may be used with confidence for the approximate comparison of viscosities of materials of the same class. A simple modification is suggested which enables a check to be made on the assumed constancy of surface tension.

*Introduction.*

ONE of the oldest works methods of obtaining an idea of the viscosity of liquid is probably that developed in the apparatus of Cochi<sup>us</sup>, in which a tube nearly full of the liquid is inverted, and the time taken by the more or less cylindrical air-bubble to travel over a certain distance is noted. The Cochi<sup>us</sup> instrument itself has been largely used in the nitro-cellulose industry, and simple forms are much used in varnish making. A short examination of the

\* Communicated by the Author. Published by permission of the Aeronautical Research Committee.



influence of diameter of tube and length of bubble on the rate of rise has been published by Faust (*Zeits. Phys. Chem.* xciii. p. 758, 1919), who used a very viscous oil for his experiments. An elaboration stated to be suitable for use with oils having viscosities varying from 0.15 to 0.9 poise has been described by Abrams, Kavanagh, and Osmond (*Chem. and Met. Eng.* xxv. p. 665, 1921). Gardner and Holdt (*Circ. No. 128 of Paint Manufacturers' Association of the U.S., 1921*) advance suggestions for the application of the method in varnish works, involving the use of a set of standard tubes containing oils of known viscosity from about 0.5 to 5.5 poises, the viscosity of the sample being estimated from that of the standard which gives most nearly the same rate of rise. None of these authors appear to have recognized that the surface-tension of the liquid must, at least in some circumstances, play a part in determining the rate of rise of the bubble. This influence will be discussed later.

A number of experiments have been made in connexion with this type of viscometer in order to obtain some idea of the limitations to which it is subject.

#### *Influence of size of Bubble and Tube.*

The effects of length of bubble and of diameter of the tube were first investigated in the case of water, and in this series it was decided to avoid, as far as possible, errors due to variation in cross-section of the tube at different points. With this end in view, the time required for the flow of 100 c.c. of water past the bubble was measured, the velocity being adjusted by suitable variation of the head so that the bubble remained practically stationary in the vertical tube instead of rising as in the case of the Coehus or Abrams viscometer. The water was taken from the mains, and its temperature varied by only negligible amounts throughout the series. Care was taken to adjust the velocity of flow towards the end of a run so that the surface of the bubble returned exactly to the original position. The times observed were fairly concordant, varying by 1.5 per cent. as a maximum (except in the smallest tube, where the differences amounted to 10 per cent.): in general about four determinations were made, so that the means are probably subject to an error of not more than 0.3 per cent. The diameters of the tubes were subsequently measured by weighing the mercury which filled a length of some 10 cm. in the neighbourhood of the bubble. The following table contains the results given by three

tubes; it was not found possible to keep a bubble stationary in a tube of diameter 0.58 cm.

Diameter of tube.	Length of bubble.	Mean time required to collect 100 c.c.
0.633 cm.		308 secs.
0.652 ..	2.2 cm.	225.3 ..
	5.1 ..	226.2 ..
	16.2 .	225.1 ..
1.00 ..	1.0	20.1 ..
	2.0 ..	19.4 ..
	5.5 ..	19.2 ..
	12.0 ..	19.4 ..

Although this table clearly demonstrates that the diameter of the tube has a very large effect on the rate of flow of water past the bubble, the deliveries do not vary even approximately as the fourth powers of the diameters as was found by Faust for his oils: the product, time of flow of 100 c.c.  $\times$  (diameter of tube)<sup>4</sup>, amounts for the three tubes to 49.6, 40.6, and 19.3 respectively. His conclusion as to the absence of any effect due to length of bubble is, however, confirmed by these experiments, at any rate for bubbles having a length greater than the diameter of the tube.

#### *Relation between Rate of Rise and Viscosity.*

In a second series, tubes were set up as viscometers of the Coehius type: marks were etched 10 cm. apart and each about 7 cm. from the end of the tube. One end of the tube was sealed and the other end closed, after introduction of the liquid to be used, by a well-fitting glass rod and rubber tubing. The viscometer tube was fixed into the corks at either end of a water-jacket of which the temperature could be adjusted electrically. By means of two sets of levelling screws on a brass plate attached to the water-jacket it was possible to arrange that the tube should be vertical whichever end was uppermost when the screw-points rested on a suitably shaped horizontal plate, and that no further adjustment should be necessary after inversion. The temperature was kept constant at 25° C. It was again verified that the length of the bubble was without appreciable influence on the results, and, except where otherwise stated, a length of about 2.5 cm. was used.

When the diameter of the tube was 0.478 cm., water gave times of rise of the bubble through 10 cm. which varied very considerably *e.g.* from 103 to 182 secs.; a 2.5-cm. bubble gave a mean time (mean of 14) of 147 secs., a 1.2-cm. bubble a mean time of 136 secs. A glycerin solution of sp. gr. 1.02 (viscosity about 1.2 centipoises) gave a time 1283 secs. With oils much better concordance was obtained, and duplicates agreed generally within 1 per cent. The following figures were obtained :—

Oil.	Viscosity.	Time of rise of bubble.	$\frac{\text{Viscosity}}{\text{time of rise}} = (1).$	$\frac{(1)}{\text{density}}$
Singer .....	0.144 poise	27.3 secs.	0.00528	0.00622
Machine.....	0.609 „	107.7 „	0.00565	0.00636
Dynamo.....	3.07 „	496.0 „	0.00612	0.00660

In a tube of diameter 0.652 cm. the following observations were made, the duplicates being again accordant :—

Liquid.	Viscosity.	Time of rise.	$\frac{\text{Viscosity}}{\text{time of rise}} = (2).$	$\frac{(2)}{\text{density}}$
Machine oil.	0.609	4.4 secs.	0.138	0.155
Dynamo „	3.07	18.6 „	0.165	0.178
Castor „	6.51	41.0 „	0.159	0.166
Glycerol ...	6.31	55.6 „	0.113	0.090

The viscosities given in the second column were determined by an absolute method and by means of calibrated Ostwald tubes (Rep. and Mem. of Aeronautical Research Committee, No. 906, 1923).

Though a rough proportionality between the viscosity and time of rise is apparent in either of the above tables, there are variations of 15 to 40 per cent. in the “constants” of column 4. The variations are not systematic, *i.e.* the constant does not increase regularly with the viscosity; nor is any improvement effected by making the obvious replacement of viscosity by kinematic viscosity as has been done in the last column. From the fact that the most marked discrepancy occurs between the figures for glycerol and for the oils in the second table, it seems possible that the surface-tension may be of importance, since glycerol has a surface-tension considerably different from that of oils.

*Theoretical.*

Dimensional analysis of the problem leads to equations such as

$$v = \frac{d^2 \rho g}{\eta} \cdot f\left(\frac{d^2 \rho g}{T}, \frac{d^3 \rho^2 g}{\eta^2}, \frac{l}{d}\right), \quad \dots \quad (1)$$

where

$v$  is the linear velocity of rise of the bubble ;

$l$  „ length of the bubble ;

$d$  „ diameter of the tube ;

$\rho$ ,  $\eta$ , and  $T$  are the apparent density (in air), the viscosity and the surface-tension of the liquid ;

$g$  is the acceleration due to gravity.

In this form the equation is of little assistance, but we may introduce certain limitations which render it more simple. For the type of motion with which we are dealing, it has been shown that the length of the bubble is without influence on the velocity, so that we may neglect  $l/d$  in the function in brackets. It is also clear, from the experiments, that to a first approximation  $v \propto \frac{l}{\eta}$ , so that the kinetic energy

terms are unimportant ; the function  $\frac{d^3 \rho^2 g}{\eta^2}$  is, in fact, convertible to Reynolds's criterion by multiplying it by  $\frac{\eta v}{d^2 \rho g}$ , so that if the motion be sufficiently slow, this function may be regarded as a constant, from analogy with the laws of ordinary viscous flow. Hence it appears reasonable to inquire whether the simplified formula

$$v = \frac{d^2 \rho g}{\eta} f\left(\frac{d^2 \rho g}{T}\right) \quad \dots \quad (2)$$

will accord with the experimental facts.

The function  $f\left(\frac{d^2 \rho g}{T}\right)$  which occurs on the right-hand side will be more readily recognized in the form  $\phi\left(\frac{\tau}{a}\right)$ ,

which is more usually employed in surface-tension problems, to which it is equivalent since  $T = 1/2 a^2 \rho g$ , where  $a^2$  is the specific cohesion. The function is thus related to the shape of the portion of the bubble concerned, *i. e.* of the rear end. Faust's measurements on two very viscous oils indicate that in tubes of 1.6 to 2.4 cm. diameter the linear velocity is very nearly proportional to  $d^2$ , decreasing only by some 2 to 5 per cent. more than it should for strict proportionality. He

gives no measurements of the surface-tension, but at room temperatures most mineral oils have a value of about 0.267 cm. for  $a$ , so that  $r/a$  in these cases lies between about 3.0 and 4.5. The decrease in velocity below that required by the relation  $v \propto d^2$  becomes more marked in the smaller tubes; it amounts to 13 per cent. in his smallest tube of diameter 1.2 cm., for which, assuming the above value of  $a$ , the ratio  $r/a$  was 2.3.

With the smaller values of  $r/a$  which occur in the measurements recorded above for four different oils, the function by which  $\frac{d^2 \rho g}{\eta}$  has to be multiplied to give the observed velocity of rise is found to be much smaller. In this connexion the surface-tensions of the oils in question and of the sample of glycerol used were measured by the drop-weight method, using the precautions and factors indicated by Harkins and Humphrey J. Am. Chem. Soc. xxxviii. 228, 1916 and xli. 518, 1919; the values obtained for the  $\sqrt{\text{specific cohesion}}$  at 25° C. were

	$a$ .	$\frac{0.652}{2a}$ .	$\frac{0.478}{2a}$ .
Singer oil	0.265	—	0.90
Machine „	0.266	1.22	0.90
Dynamo „	0.272	1.20	0.88
Castor „	0.281	1.16	—
Glycerol ...	0.325	1.03	—

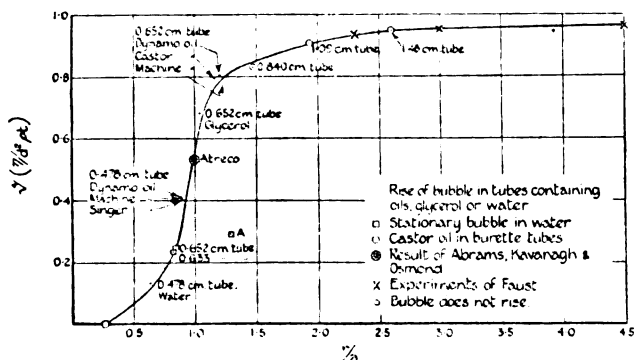
The values of  $r/a$  in these experiments thus extend from 0.88 to 1.22, and it is obvious from the experimental results that the value of  $f\left(\frac{d^2 \rho g}{\eta}\right)$  increases very rapidly with  $r/a$ . Thus the “constants” (viscosity/time of rise) for the two tubes, taking the figures for machine oil and dynamo oil, are related, not as  $d^2$ , but roughly as  $d^2 \times (d^2)^{4.15}$ .

The values obtained experimentally for  $\sqrt[4]{\frac{\eta}{d^2 \rho t}}$  (where  $t$  is the time required for the bubble to rise 10 cm.), i. e. for  $\sqrt[4]{\left(\frac{\eta v}{d^2 \rho g} \cdot \frac{g}{10}\right)}$ , have been plotted against  $r/a$  in the accompanying diagram (fig. 1), the fourth root being used merely for convenience in reducing the scale. Corresponding values have been deduced from the experiments with the

stationary bubble in water. In order to get an idea of the form of the curve over a larger range of  $r/a$ , the following further observations were made :—

(a) In a tube of small enough diameter containing liquid a bubble is found not to rise at all ; possibly there might be a slow rise if the walls were perfectly wetted, but this would appear to be infinitely slow. The limiting value of  $r/a$  was deduced approximately by using acetone, benzene, chloroform, water, etc. in tubes of various sizes, as about 0.27 ; but the exact limit seems to depend on other factors, so that this figure may be in error, for a particular liquid, by say  $\pm 0.04$ .

Fig. 1.



(b) Faust's results, already quoted, indicate that the curve becomes practically horizontal at high values of  $r/a$ , the function here plotted increasing by some 2.1 per cent. between  $r/a=2.3$  and  $r/a=3.0$ , and by only 1 per cent. between  $r/a=3.0$  and  $r/a=4.5$ . The gap between these figures and those above recorded was bridged by some rough determinations, at "room" temperature, of the rate of rise of bubbles in burette tubes of diameters 0.840, 1.096, and 1.41 cm. containing castor oil ; the viscosity of the castor oil at the prevailing temperature was deduced from the known Redwood times by Higgins's formula, using temperature coefficients derived from Kahlbaum and Räber's table ; the value for  $a$  was taken as 0.285 cm. The points so found are indicated by circles. After drawing a smooth curve through the whole of the points obtained, the curve was

extrapolated by identifying the value of  $\sqrt[4]{\left(\frac{\eta}{d^2rt}\right)}$  for the oil used by Faust at  $r/a=2.3$  with that given by the curve,

and calculating the corresponding values indicated by his results for  $r/a = 3.0$  and  $r/a = 4.5$ .

The point marked Atreco is derived from the statement by Abrams, Kavanagh, and Osmond (*loc. cit.*) that the factor to convert to "Saybolt seconds" the times of rise of the bubble in the bubble viscometer described by them is approximately 10, the factor increasing with the viscosity if the diameter of the tube is more than 0.53 cm., and decreasing with the viscosity if the diameter is less than 0.52 cm. Applying the Saybolt conversion formula  $\eta/\rho = 0.00213t - 1.535/t$  to any one of the oils mentioned by them as used for calibration, and assuming the factor 10 to be correct for a diameter of 0.525 cm., the value of an ordinate may be deduced corresponding with a value of  $r/a$  of 0.99, where  $a$  is taken as 0.265 cm. for the temperature of 100° F. at which they worked. The point is found to agree well with the curve; the closeness of the agreement must be regarded as somewhat fortuitous in view of the assumptions necessary.

The position of the point A, which represents the rate of rise of a bubble in water in a 1-cm. diameter tube, may serve as a reminder of the limitations we have introduced into the dimensional method. When the viscosity of the liquid is low and the rate of rise high, due to the use of a wide tube, *i. e.* to the existence of a fairly high ratio of  $r/a$ , there is an obvious change in the form of the bubble, especially at its lower end. For the slowest movements (viscous liquids with  $r/a < 1.1$ , or mobile liquids with  $r/a < 0.7$ ) the two ends of the cylindrical bubble appear roughly hemispherical, the thickness of the film of liquid on the walls being otherwise uniform from top to bottom, as far as can be seen. As the rate of rise increases, owing either to reduction in viscosity or increase in  $r/a$ , the top of the bubble becomes more elongated (bullet-nosed) and the rear end more flattened; the flattening of the rear end is accompanied by the development of a short neck at about 1 diameter length above its lowest point, where the thickness of the film on the wall is several times as great as either just above or just below; this stage is illustrated in figs. 2 A and B (Pl. VI.). This neck becomes gradually longer as the velocity of the bubble is increased (*cf.* fig. 2 C): about this stage, kinetic energy terms may presumably begin to form an appreciable fraction of the viscous losses. At still higher velocities the change of curvature may appear at 3 or 4 diameters above the bottom of the bubble, and the relative increase in thickness of the film becomes less. In a slightly wider tube the thickened

film itself breaks up into one or more further thickened rings with thinner layers between them; such a stage is illustrated in fig. 2 D, corresponding with point A, where, however, the full number of rings cannot be distinguished as well as by visual examination of the bubble. In a tube of say 2 cm. diameter containing water the bubble shows no thickening of the film, but it is obvious that the motion is no longer steady, for the flattened base of the bubble does not remain symmetrical about the axis of the tube.

This last observation is interesting as being the extreme indication of the labile nature of the phenomenon discussed. Anyone who has noticed the rise of a bubble in a tube will have recognized that the steady flow, occurring when the tube is vertical, is metastable, the rate of rise increasing very rapidly for small deviations from the vertical. The apparent stability is conditioned by the viscous damping forces; and when these are reduced by increasing the diameter of the tube the system reverts to its normally unstable state where the thickness of the liquid film is not uniform round the circumference and the viscous resistance offered is less than for the uniform film.

The more complicated conditions of flow which occur when the kinetic energy terms are not negligible are reflected in the fuller dimensional formula

$$v = \frac{d^2 \rho g}{\eta} f \left( \frac{d^2 \rho g}{T}, \frac{d^3 \rho^2 g}{\eta^2}, \frac{l}{d} \right). \quad (1)$$

This formula indicates at once that the flow is not fixed solely by the value of  $r/a$ , but that the function also involves kinetic energy terms and possibly also the ratio of  $l$  to  $d$ .

### Conclusion.

There is a very large number of "practical" cases in which the viscosity (of a lubricating oil or of a varnish for example) does not require to be known more accurately than to some 5-10 per cent. The above measurements and theoretical discussion show that so long as there is a close concordance between the surface-tensions of the liquids compared, and the diameter of the tube selected is such as to give a suitably slow rate of rise, the time required for the bubble to travel over a given distance is proportional, within an error of less than this amount, to the kinematic viscosity. The comparison of viscosities is least affected by surface-tension when the viscosities are so high that wide tubes may be employed, such that the value of  $r/a$  is above about 2.0. If it is desired to make use of the method for



liquids of lower viscosity (0.2 to 5 poises), it is necessary to recognize that very serious error may be occasioned by a small difference in surface-tension (see below). For liquids of viscosity less than, say, 0.1 poise the scheme is quite unsuitable, particularly when, as with aqueous solutions, the surface-tension is high and may be greatly depressed by impurities to an extent depending on the rate of absorption of solute at the air-liquid interface; with such low viscosities the diameter of the tube necessary to secure the required slow rate of rise becomes so small that unavoidable variations of diameter are liable to render the rise irregular owing to their large effect on the ratio  $r/a$ . In works and other places where one type of liquid only is handled, it may frequently be sufficient to assume that the surface-tension remains constant. But it will generally be more satisfactory to supplement the "viscosity" determination by a comparison of the surface-tensions, which may readily be carried out on the same sample of liquid if the bubble tube be provided with a capillary tip so that the number of drops corresponding with the volume contained between the fiducial marks may be counted. The external diameter of the capillary should be in accordance with the suggestions of Harkins and Humphrey (*loc. cit.*), *e.g.* about 0.55 cm. for oils such as those used above, and its length and internal diameter such as to cause the drops to be formed not faster than, say, one per 10 secs.

The curve illustrates well the enormous effect of the diameter of the tube upon the rate of rise of the bubble under certain conditions. For tubes of the diameter used by Abrams, Kavanagh, and Osmond (*loc. cit.*) with oils having  $a=0.265$  cm., the relative time of rise of the bubble is indicated as decreasing some twelve to fifteen times as fast as the relative increase in diameter\*. Since the

\* In the neighbourhood of  $r/a=1.0$  the curve approximates to a straight line having the equation  $\sqrt[4]{\left(\frac{\eta}{d^2\rho t}\right)} = K\left(\frac{r}{a} - c\right)$ , where  $K$  and  $c$  have numerical values about 2 and 0.7 respectively. Hence

$$\frac{dt}{t} = - \frac{2(3\frac{r}{a} - c)}{\frac{r}{a} - c} \frac{dr}{r}, \text{ and assuming } \frac{r}{a} = 1 \text{ and } c=0.7, \text{ we have}$$

$dt/t = -15 dr/r$  at this point. Similarly when  $r$  is constant,

$$\frac{dt}{t} = \frac{4\frac{r}{a}}{\frac{r}{a} - c} \cdot \frac{da}{a}, \text{ so that, taking the above values for } r/a \text{ and } c,$$

$$\frac{dt}{t} = 13.3 \frac{da}{a}. \text{ Hence } \frac{dt}{t} = 6.6 \frac{d\Gamma}{T}.$$

diameter was only 0.525 cm., this would mean that a variation in diameter of 0.001 cm. would change the time of rise of a bubble by some 2.5 per cent. It is thus of little use to specify the viscosity by stating a certain time of rise in a tube of specified diameter in this range, but each tube should be calibrated by means of suitable standard liquids of appropriate viscosity.

The effect of differences in surface-tension on the rate of rise of a bubble in a tube of fixed diameter may also be very large. With oils in the "Atreco" viscometer the percentage change in rate of rise (*i. e.*, in indicated viscosity) may be some six or seven times the percentage change in surface-tension. The effect is shown to diminish very rapidly with increase in diameter of the tube, *i. e.* when the viscosity of the liquid examined is so high as to allow such an increase to be made without unduly increasing the velocity.

Gardner and Holdt (*loc. cit.*) do not give details sufficient to allow their results to be interpreted on the curve here obtained; but since their viscosity range is higher and their tubes wider, it would seem that  $dt/t$  is only about three times as great as  $dr/r$ : they suggest that  $dr/r$  should be not more than 5 per cent. to give the reproducibility at which they aim, which is presumably not better than  $\pm 15$  per cent. in view of the rapid rise with which they appear to work. In these wide tubes the surface-tension is relatively unimportant.

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XXXII. *The Production of some Spectra of Carbon, Oxygen, and Nitrogen in the Presence of Neon.* By W. H. B. CAMERON, M.Sc., Research Student, Queen's University Belfast\*.

A NUMBER of recent papers have described modifications of spectra produced by admixture of substances with the inert gases, and in this respect the action of Helium was particularly notable. In connexion with Carbon † spectra there is the production of the Comet-Tail bands and of the Negative Carbon bands with great intensity, the isolation of the Triplet System, and under other conditions, of the arc lines of Carbon. More recently Merton and Pilley ‡ have demonstrated a strong development of the

\* Communicated by Dr. R. C. Johnson, B.A., Ph.D.

† Proc. Roy. Soc. A. ciii. p. 383 (1923); & cviii. p. 343 (1925).

‡ Phil. Mag. [6] l. p. 195 (1925); Proc. Roy. Soc. A. cvii. p. 411 (1925).

Negative bands of Nitrogen, and have also isolated the arc lines of this element in high-pressure Helium. A year ago, an investigation was made by Dr. Johnson and myself of the action of Argon on spectra \*. The present communication describes similar work in connexion with Neon.

*The Effect of Neon on Carbon Spectra.*

*Swan bands and Triplet System.*—The discharge-tubes which were used in this investigation were of the usual H pattern, having a bore of about 15 mm., each being furnished with carbon electrodes, quartz window, palladium regulator, and side bulbs containing caustic potash and phosphorus pentoxide. A charcoal trap immersed in liquid air was employed to purify the neon. In view of the action of both helium and argon in developing the Swan bands rather than the Angström bands when carbon is present as an impurity, it was not surprising to find that neon behaved in a similar manner, and that on admitting hydrogen, the Triplet System was isolated as in the case of the two inert gases mentioned.

*Comet-Tail bands.*—The production of the comet-tail bands in high-pressure helium, a phenomenon which has no counterpart in the case of argon, has already been noted, and steps were taken to ascertain whether neon was capable of producing this spectrum. A discharge-tube containing neon at a pressure of 25 mm. was run for a considerable time in order to reduce the quantity of carbon present. After several hours the glow began to assume the red colour of neon and striæ appeared along the tube. When examined with the spectroscope, this showed the neon lines and the comet-tail bands. Their isolation from the other familiar band spectra of carbon in the visible region was complete. This development of the system was not as intense as that in helium but was equally definite. The band in the red at  $\lambda\lambda$  6246, 6196 was present precisely as in helium, though somewhat confused in this case with the strong neon lines in the neighbourhood. A system of bands associated with the comet-tail bands is recorded by Johnson in a recent paper (Proc. Roy. Soc. A. cviii. p. 350, 1925), and Birge † has shown that these two systems are numerically related. These bands are produced also, though rather faintly, along with the cometary bands in neon. It is perhaps worth

\* Proc. Roy. Soc. A. cvi. p. 195 (1924); Phil. Mag. [6] xlviii. p. 1069 (1924).

† 'Nature,' Aug. 8, 1925, p. 207.

mentioning that in a wide-bore tube with aluminium electrodes having less than 1 mm. of neon and only a very minute quantity of carbon, the comet-tail bands were faintly visible.

*Carbon line spectrum.*—When tubes in the above condition were subjected to a mild condensed discharge they glowed with a brilliant yellow light. Analysis showed that the greater part of this light came from neon lines, but that the cometary bands persisted faintly. A search was made for the carbon arc lines which appear under similar conditions in helium, but with the exception of  $\lambda 2478$  no trace of these could be found. Some of the doublets of C.II. were present.

*Negative Carbon bands.*—The great intensity of the negative carbon bands was a striking feature of their development in helium. In neon at similar pressures this system appeared with moderate strength together with the 3rd positive bands of carbon greatly reduced in intensity and traces of the 4th positive bands. A condensed discharge practically eliminated the 3rd and 4th positive bands leaving the negative bands outstanding, provided only a small quantity of carbon was present.

*The CH bands.*—An interesting observation was made in the case of a tube containing only a minute trace of carbon and high-pressure neon. A photograph taken on a quartz prism spectrograph revealed, along with faint traces of the comet-tail bands and the Swan head  $\lambda 5165$  a strong development of the CH band  $\lambda 4315$  and associated heads. The only other prominent features were the OH bands which appeared with moderate intensity. In every case in which the isolation of the CH band from other carbon spectra was effected, the OH bands occurred also. The tube could not have contained much hydrogen as the Balmer series was but faintly visible.

*Martin's CS bands.*—Some of the tubes which were filled with high-pressure neon presumably contained as an impurity a minute trace of sulphur. When these were in the condition described above, and were showing the CH band, they also showed Martin's CS bands quite well defined. From the conditions under which this system was observed, it would seem that its appearance furnishes the most sensitive test of the presence of sulphur if there exists also a trace of a carbon impurity (which is always difficult to eliminate). Both these phenomena could be produced equally well in high-pressure argon.

*A new band system associated with Carbon.*—An additional system of bands has been observed when uncondensed

discharges are used to excite wide-bore tubes having the usual accessory bulbs and filled with high-pressure neon. (The discharge-tubes were fitted with carbon electrodes.) These bands could not be obtained with very great intensity even with exposures of six hours. In Table I. measurements of some thirteen heads are given. Other heads were

TABLE I.

Intensity.	Wave-length. (I.A.)	Intensity.	Wave-length. (I.A.)
0	2257.7	0	2451.8
0	2259.5	1	2453.9
0	2260.3	2	2455.0
0	2261.2	2	2456.0
—	—	1	2457.8
0	2277.0	—	—
0	2278.5	1	2492.9
0	2279.6	1	2494.4
0	2280.5	1	2495.7
—	—	1	2497.5
0	2369.0	0	2510.9
0	2371.2	1	2513.7
1	2372.2	2	2514.9
1	2373.3	2	2516.2
0	2375.0	1	2517.8
1	2388.8	0	2531.9
1	2391.1	1	2534.5
2	2392.1	2	2535.6
2	2393.1	—	2536.7
1	2394.8	1	2538.6
1	2409.2	0	2553.3
1	2411.4	1	2555.9
2	2412.5	2	2557.1
2	2413.5	2	2558.2
1	2415.3	1	2560.2
0	2430.3	0	2575.3
0	2432.4	3	2577.7
1	2433.4	2	2579.1
1	2434.5	2	2580.2
0	2436.2	1	2582.2

*a*=doubtful, possibly fine structure work.

*b*=confused with the mercury line.

Other members of the system are present, but confused with structure of the third positive Carbon bands.

visible, but were too much confused with the 3rd positive carbon bands to render their measurement under this dispersion of much value. The band system as a whole is of the usual type and degraded to the red; each "head" has a somewhat complex structure embracing five sub-heads. The system was found under conditions in which the Swan bands, the

comet-tail bands, or the Triplet System appeared in the visible region, and a weak development of the negative carbon bands invariably accompanied the system. With the present available evidence, however, it is difficult to assign it to any particular molecule. It is believed that this band spectrum has not hitherto been recorded. The same bands have also been observed in helium and argon, but only very faintly.

### *Neon-Oxygen Mixtures.*

In view of recent work by McLennan and Shrum\* describing the production of the green aurora line in helium-oxygen and neon-oxygen mixtures, a special search has been made for this line under various discharge conditions. We have examined neon-oxygen mixtures of varying composition and pressure with both uncondensed and condensed discharges and in wide and narrow bore capillary discharge-tubes, but have been unable to find any trace whatever of this line. The only explanation we are prepared to offer is that possibly heavier currents are needed for its production, and we never used more than 5-10 amps. through the primary of the induction coil.

*Oxygen band spectra.*—It has been found possible to develop weakly the band spectra of oxygen with mild condensed discharges through wide-bore tubes in the presence of neon at all pressures up to 25 mm. The intensity of the ultra-violet emission bands, attributed by Johnson† to an  $O_2$  molecule, relative to that of the negative bands when produced in neon, is greater than in the normal production of these systems by condensed discharges through pure oxygen.

*Line spectrum O.I.*—In the case of wide-bore discharge-tubes, uncondensed discharges gave practically no light whatever proportions of neon and oxygen were used. Very long exposures, of course, ultimately gave the principal lines of both gases. Attention is therefore confined to condensed discharges in the case of wide-bore tubes.

With a little neon, say 1 mm., the addition of a small quantity of oxygen gave only the first members of the series of O.I. Increasing the pressure of neon up to 5 or 6 mm. gave practically no change, but neon at 25 mm. pressure had the effect of extending considerably the several series of oxygen. In the case of capillary tubes a little neon together with various quantities of oxygen brought up P(2), P(3), p(2), d(4), fairly strongly. Increasing the proportion of oxygen

\* Proc. Roy. Soc. A. cviii. p. 501 (1925).

† Proc. Roy. Soc. A. cv. p. 683 (1924).

seemed to effect a slight reduction in the intensity of  $d(4)$  under all conditions of discharge. The uncondensed discharge through a capillary tube containing high-pressure neon extended the series and, in particular, excited the higher members of the sharp and diffuse triplet series. When condensed discharges are passed through capillary tubes, the most energetic type of excitation results. In the presence of a little neon (say 1 mm.) to which oxygen was added, the most notable effect of adding more oxygen was to increase the intensity of the principal singlet series while the sharp and diffuse triplets got weaker. With 5 mm. of neon addition of oxygen produced practically no change excepting a slight enhancement of  $p(2)$ . Similarly, if the oxygen content is fixed and the neon content varied, there results little change over the range 0 to 5 mm., but high-pressure neon develops the higher members of the series well,—especially the sharp and diffuse triplets. Table II. includes most of these facts.

TABLE II.

Discharge Conditions and Bore.	Neon content.	Oxygen content.	Results.
Condensed. Wide Bore.	1 mm.	Small quantity.	Only first members visible.
	5 mm.	do.	Practically no change.
	25 mm.	do.	Series considerably extended.
Uncondensed. Capillary.	1 mm.	A little.	$P(2)$ , $P(3)$ , $p(2)$ , $d(4)$ fairly strong.
	5 mm.	do.	$d(4)$ slightly reduced, otherwise no change.
	25 mm.	do.	Higher members of Sharp & Diffuse triplets strong.
Condensed. Capillary.	1 mm.	A little.	Fairly good development of series lines. Principal Singlets enhanced; Sharp & Diffuse Singlets & Triplets reduced as above.
	5 mm.	do.	No change except slight enhancement of $p(2)$ .
	25 mm.	do.	Higher members much better developed, especially Sharp & Diffuse Triplets.

It is noteworthy that a mild condensed discharge through a wide-bore tube containing high-pressure neon and a little oxygen gives the best development of the higher members of the series in O.I. At all pressures of neon a condensed discharge is capable of bringing up the stronger members of the elementary series of oxygen in addition to the lines of the compound or series spectrum.

*Neon-Nitrogen Mixtures.*

The recent work of Merton and Pilley (*loc. cit.*) on the spectra of helium-nitrogen mixtures disclosed some interesting features. As the partial pressure of nitrogen was diminished, a stage was reached when the first and second positive band spectra disappeared and the negative bands remained, developed strongly along the whole tube. The system as thus produced was considerably extended towards the red,—a feature apparently characteristic of the production of several band spectra in helium. Similar phenomena to these have been observed in the case of nitrogen in neon, and with a trace of the former in high-pressure neon the negative nitrogen bands can be isolated with intensity. When a mild condensed discharge is passed through a tube in this condition, it yields a spectrum consisting of the neon lines and some arc lines of nitrogen. Not all the arc lines of nitrogen isolated in helium are produced in high-pressure neon. Some lines recorded by Merton and Pilley as very strong do not seem to be present, but quite a number of the arc lines of nitrogen have been identified and measured. With the comparatively small dispersion of the prism spectrograph used, it is possible that a few lines of nitrogen really present were confused with strong neon lines. Table III. gives a list of all the nitrogen arc lines identified

TABLE III.

Nitrogen arc lines.	Intensity in Helium.	Intensity in Neon.	Nitrogen arc lines.	Intensity in Helium.	Intensity in Neon.
6874.3	1	1	4305.5	6	3 d
6653.5	4	4	4253.3	3	2
6484.9	8	4	4230.4	4	3
4935.0	9	4	4223.1	5	3
4914.9	4	1	4215.0	—	3
4750.2	2	2	4137.6	4	3
4492.4	5	2 d	4113.9	5	2
4358.3	7	2	4099.9	9	9
4336.5	4	7	4011.0	4	1
4317.7	4	2	4000.0	3	1
4313.1	3	2 d			

d=diffuse.

by the complete measurement of a single plate taken under the above conditions. None of the spark lines of nitrogen were visible. The intensities of such arc lines as appear are in many cases in agreement with those of Merton and Pilley for the lines in helium. There are, however, some intensity



changes too obvious to admit of any doubt, and there are many strong lines attributed to nitrogen which we have not been able to produce in our experiments with nitrogen-neon mixtures. On the other hand, there are a number of lines which we have been unable to identify as arising from impurities, and it seems just possible that they may belong to the arc spectrum of nitrogen. The approximate measurements of these, as far as we have determined them roughly from one plate, are :—

6992.5 (5) ; 6425.1 (2) ; 6004.7 (3) ;  
4216.1 (4) ; 4024.6 (2) ;

In the event of any theoretical work pointing to this origin it should be possible to measure these up accurately.

### *Discussion.*

We have now available for the first time, data relating to the production of some spectra of carbon, oxygen, and nitrogen in all three inert gases, viz., helium, neon, and argon, and a discussion of their comparative behaviours would not seem superfluous. For the sake of clearness a summary of these data is presented in Table IV.

TABLE IV.

System.	In Helium.	In Neon.	In Argon.
Comet-Tail bands.	Strong.	Less strong.	Absent.
Associated bands.	Fairly strong.	Weak.	Absent.
Negative O bands.	Very strong.	Moderately strong.	Very weak.
Carbon arc lines.	Present.	Absent.	Absent.
Negative N bands.	Strong.	Strong.	Absent.
Nitrogen arc lines.	Present.	Present in part.	Absent.
Triplet System.	Present.	Present.	Present.
Ultra-violet Oxygen bands.	Weak.	Weak.	Absent.
Negative Oxygen bands.	Fairly strong.	Very weak.	Absent.
O.I. ....	Present.	Present.	Present.
O.II. ....	?	Strong members present.	Absent.

In the paper of Merton and Pilley already mentioned, the authors put forward an interesting suggestion to explain the phenomena of the development of certain arc spectra in

the inert gases. Briefly expressed, the theory states that the presence of any inert gas in large excess increases the expectation of life of the neutral atom from which the spectrum arises, and at the same time allows the passage of a heavy current. Added to these effects there is a limit placed by the resonance potential of the inert gas used to the energy which may be acquired by the bombarding electrons during the passage of a condensed discharge. The critical potentials of helium, neon, and argon are as follows:—

<i>Gas.</i>	<i>Resonance.</i>	<i>Ionization.</i>	<i>Author.</i>
He.....	20·4	25·6	Franck & Knipping
	21·2	25·3	
Ne.....	11·8	21·5	Hertz.
	17·8		
A .....	11·5	15·1	Horton & Davies.

The nitrogen arc lines appear well in helium, some appear in neon, but they are absent in argon. In accordance with the above theory this would suggest that the excitation potential of the N.I. spectrum lies in the neighbourhood of 11·8 volts. The lines of N.II. are not found in the presence of any of these inert gases, and consequently this excitation potential must lie above 20·4 volts. This is in agreement with Miss Payne's estimated value of 24 volts for the second ionization potential of nitrogen, after the first electron has been removed.

In the case of carbon line spectra difficulties present themselves. The carbon arc lines appear in helium only, but some of the spark lines are unmistakably present in both helium\* and neon. The first difficulty is connected with the non-appearance of the arc lines of carbon in neon when it is remembered that some spark lines appear. Moreover, Saunders has suggested that the first ionization potential of the neutral carbon atom may be 7 or 8 volts, and this would allow of the production of the arc lines in all three inert gases. The second difficulty arises when we attempt to explain the presence of such spark lines as do appear. The highest energy level to which the second electron must be raised in order to radiate the lines observed in helium is the 5( $\phi$ ) level. This would require a 22·1 volts† impact on an ionized carbon atom, which is clearly disallowed by the above theory.

\* Proc. Roy. Soc. A. cviii. p. 343 (1925).

† Calculated from Fowler's value for the series limit: Proc. Roy. Soc. A. cv. p. 299 (1924).

As regards the first problem mentioned, any explanation at the present time must be of a very speculative nature. It is suggested that the manner of breaking down of the molecule which contains the carbon atom and the potential at which this occurs are of more fundamental importance than the actual excitation potentials of the line spectra. Thus at the comparatively low voltages obtainable in neon the compound may break down and yield as one of the products only *ionized* carbon atoms, which are then available as sources of the spark spectrum, and at higher voltages such as may be obtainable in helium only it may break down in a different manner yielding in addition neutral carbon atoms from which arises the arc spectrum. Before applying to the case of nitrogen for which some data are available, a further suggestion will be made which may help to elucidate the second difficulty pointed out. Examination of a plate showing the carbon arc lines developed in the presence of high-pressure helium revealed the fact that the complete arc spectrum of the inert gas was produced. The significance of this is obvious. While it is admitted that the probability of a *free* electron acquiring energy above the first resonance level of helium is very remote, it is clear that the electrons in many helium atoms must be raised to much higher energy levels. This is probably due to secondary collisions and to "photo-impact." It seems reasonable to assume that these excited helium atoms may impart their energy to carbon atoms if such are in the neighbourhood, so that the latter may be excited up to the *ionization* level of helium. The same reasoning would hold in the case of the other inert gases. Under particularly energetic conditions it may be possible to exceed this limit. This was proved in the case of high-pressure argon in a capillary bore tube, excited by a heavy condensed discharge, when the blue spectrum of argon was developed. It was interesting to note that some of the carbon-spark doublets appeared faintly under these conditions.

On this modification of Merton and Pilley's view,—viz., that under moderate discharge conditions energy up to the first ionization potential is available, and under more energetic conditions even above this limit,—it is possible to explain in some degree most of the phenomena recorded above. Since the ionization potential of C.II. is 24.3 volts and that of helium and neon 25.6 and 21.5 respectively, it should be possible to develop the spark spectrum of carbon completely in helium and partially in neon provided ionized carbon atoms are present. In helium, all the doublets above

$\lambda\lambda$  2746, 2747 have been recorded with the exception of that at  $\lambda$ 4267, and the majority of the remaining members are in the extreme ultra-violet. It still remains to be explained, however, why some of the pairs whose radiation is energetically possible do not occur in the presence of helium. In neon the same C.II. lines are recorded as in helium with the possible exception of  $\lambda$  2992, at which position there is a neon line. This is unfortunate, as the fact of the presence or absence of this C.II. line would be a test of the truth of the above assumption, since its excitation potential is 22.1 volts. All the lines which do occur have excitation potentials below the ionization potential of neon.

Reverting to the case of nitrogen, we note that Smyth\* has found critical potentials for this molecule at 16.9, 24.1, and 27.7 volts, which he interprets as corresponding to the changes :



respectively. A breakdown of the first type would be possible under moderate discharge conditions in helium and neon but not in argon, and would yield ionized nitrogen molecules. It is very probable that when these are excited the negative band spectrum† of nitrogen results, and this accounts for its appearance in helium and neon in contrast with argon. The second reaction leads to the formation of neutral nitrogen atoms, which may then be excited to give the arc lines of nitrogen. This breakdown would be possible only in helium, but under energetic conditions might be obtained to some degree in neon. It has been recorded in the present paper that during the development of the arc lines of nitrogen in neon the discharge-tube glowed with a brilliant yellow light, so that it is possible that some neon atoms were excited above the first ionization level. This may explain the partial development of the arc spectrum of nitrogen in neon. From the third reaction are liberated ionized nitrogen atoms which are capable of giving the spark lines, but this reaction could take place in helium only if conditions are energetic enough to pass the first ionization limit. Indeed, Merton and Pilley found that some spark lines appeared if intense discharges were used, but under moderate conditions they were absent. It is stated at the beginning of the discussion in accordance with Merton and Pilley's interpretation of experimental results, that the

\* *Proc. Roy. Soc. A.* civ. p. 121 (1923).

† *Cf.* origin of negative carbon bands.

#### 416 *Spectra of Carbon, Oxygen, and Nitrogen in Neon.*

excitation potential of the N.I. spectrum probably lies in the neighbourhood of 11·8 volts, but as these results have been explained alternatively this statement cannot now be sustained. It must, of course lie below the ionization potential of helium.

According to the view put forward above, it would now appear that the inert gas used plays several parts in the production of spectra requiring the ionization or complete disruption of a molecule.

(1) It limits the energy available for breaking down the molecule.

(2) It conserves the products of disruption as explained by Merton and Pilley.

(3) It limits the energy available for exciting these products.

It is suggested that energy is imparted to the gas, which is present only in small quantities, not so much by direct electron impact as through the medium of the excited atoms of the inert gas.

It will be noticed that the presence of the inert gas permits of the production of such spectra as have been dealt with in two stages, and this may account for the ease with which they are developed by this method. Under the ordinary method of producing, say, the negative band spectrum of Nitrogen from low pressure Nitrogen, it seems inevitable that sufficient energy must be imparted by a *single* electron collision (a) to ionize the Nitrogen molecule; (b) to excite this ionized molecule.

A similar explanation would appear to hold in the case of *uncondensed* discharges through high-pressure inert gas. For example, the comet-tail bands and associated bands and the negative carbon bands, all of which arise from a  $\text{C}^+\text{O}^+$  ion\*, may be developed in two stages just as the negative nitrogen bands are produced. The inert gas again probably imposes a limit to the energy available for exciting spectra, but in the absence of experimental data it is difficult to assign the limit with certainty.

It is perhaps worthy of note that in the case of helium and neon at high pressure and excited by uncondensed discharges, the arc spectrum of the gas is developed, but in the case of argon under similar circumstances, few if any of the lines of the inert gas are produced, the arc spectrum being replaced by a blue continuous spectrum. What the

\* Birge, 'Nature,' Aug. 1st, 1925, p. 170, and Aug. 8th, 1925, p. 207.

significance of this may be is not clear, but it would seem to suggest that the argon atoms possess very little energy which is capable of transference to molecules of other gases present. This may explain the inactivity of argon in the development of spectra which are produced well in neon and helium.

I wish in conclusion to express my sincere thanks to Dr. R. C. Johnson, under whose supervision the work was carried out.

XXXIII. *The Character of the Ionization produced by Spraying Water.* By P. J. NOLAN, M.Sc., Ph.D., University College, Dublin\*.

**I**N an examination of the electrification caused by spraying water, J. J. Nolan† came to the conclusion that the ionization produced consisted of a number of groups of ions having distinct mobilities. These groups were spread out over a very wide range, the mobility values extending from about the value attributed to ordinary "small" ions to that found for the Langevin or "large" ions. Similar groups of ions were discovered by J. A. McClelland and P. J. Nolan in the ionization produced by bubbling air through mercury. Further work gave corresponding results in the case of ionization produced in air bubbled through alcohol and also in air passed over phosphorus‡. The alcohol and phosphorus ions corresponded very closely, the groups being about twice as numerous as in the case of the ions derived from spraying water. In the case of the larger ions the ratio between successive mobilities was about 3·4 for the water spray and 1·8 or  $\sqrt{3\cdot4}$  for the other sources of ionization. There was fair agreement between the mobility values of the groups of ions produced in different ways, certain ions, for example those of mobilities ·00033, ·0012, and ·0041 cm./sec/volt/cm., being found in every case. In all these experiments the McClelland method of measuring mobilities was used.

The existence of these distinct groups of ions was called in question by Blackwood§. In his experiments the

\* Communicated by Prof. J. J. Nolan, M.A., D.Sc.

† J. J. Nolan, Proc. Roy. Irish Acad. xxxiii. (A) p. 9 (1916).

‡ J. A. McClelland and P. J. Nolan, Proc. Roy. Irish Acad. xxxiii. (A) p. 24 (1916); xxxiv. (A) p. 51 (1918); xxxv. (A) p. 1 (1919).

§ Blackwood, Phys. Rev. xvi. p. 85 (1920).

ionization was produced by spraying water and by passing air over a hot platinum wire, and the nature of the ionization was examined by the Zeleny divided-electrode method. Blackwood held that his results showed that the sizes of the ions produced in these cases were spread out evenly over a wide range; in other words, he found "a continuous spectrum of mobilities and not a band spectrum." The present writer\*, however, using the Zeleny divided-electrode method produced convincing evidence of the group character of the ionization due to alcohol and phosphorus and gave reasons for Blackwood's failure to obtain this result.

The question has been reopened by Busse †, who failed to detect ion-groups using both the single-electrode and the divided-electrode methods and producing the ionization by spraying water. He states that he has clearly proved that the ions produced by breaking up water cannot be classed in distinct groups but distribute themselves continuously and without gaps over a range the limits of which can be established by determining the largest and the smallest ions present. He is further of opinion that the step-like character of the ionization produced by other methods is extremely doubtful. The present writer considers that in the case of alcohol and phosphorus the evidence already produced for the group character of the ionization is unassailable. As the discontinuity of the ionization due to spraying water has only been shown by the single-electrode method in the earlier experiments, the work described in this paper was undertaken with a view to a further examination of the spray ions by the Zeleny method, which on account of its superior resolving power is specially suited to determine the points at issue.

#### *Experimental Method.*

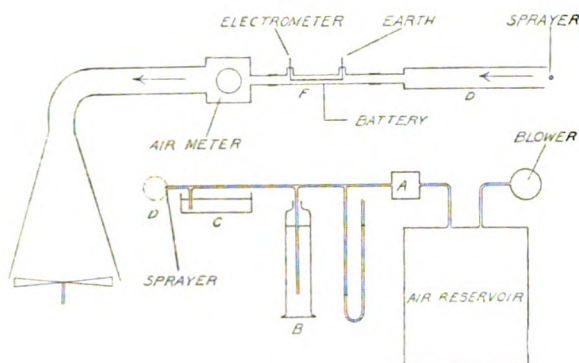
The experimental arrangements varied considerably in the course of the work. It was found that the character of the results depended a great deal on the type of sprayer used. Practically all the results which are quoted were obtained with the arrangement finally adopted which is now described. Fig. 1, the upper part of which is approximately to scale, gives a diagram of the apparatus. A rotary pump forced an air blast, the fluctuations of which were damped by a large air reservoir, through a cotton-wool plug A. The air thus purified, actuated a de Vilbiss sprayer which

\* P. J. Nolan, *Phys. Rev.* xviii. p. 185 (1921).

† Busse, *Ann. der Phys.* lxxvi. p. 493 (1925).

drew distilled water from the vessel C. This vessel had a large cross-section, and as the consumption of water by the sprayer was small, the level of the water in C did not change appreciably during an experiment. The spraying pressure was kept constant by inserting a side tube which opened beneath the surface of mercury in the cylinder B. The pump was worked at such a rate that air bubbled continually through the mercury in B. This device for keeping the pressure constant was at a distance of about 150 cm. from the sprayer. Test experiments showed that ions due to air bubbling through the mercury could not be detected in the measuring apparatus. The sprayer was

Fig. 1.



placed with its nozzle close to the end of the tube D so that the spray was at right angles to the axis of the tube. A fan driven by a synchronous motor drew a constant air stream through the tubes D and F, the latter being the Zeleny condenser with divided electrode. The quantity of air passing per second was measured by means of an air-meter.

The dimensions of the Zeleny apparatus were as follows :—

Internal diameter of outer tube ( <i>b</i> )	=	3	cm.
External diameter of electrode ( <i>a</i> )	=	·95	cm.
Length of insulated electrode	=	5	cm.
"    "    earthed electrode	=	10	cm.
Total length of electrodes + gap ( <i>L</i> )	=	15·2	cm.

The volume of tube D and its connexion up to the end of electrode was 1450 c.c. The air-current in most of the experiments was 670 c.c. per sec. The insulated electrode was connected to a Dolezalek electrometer giving

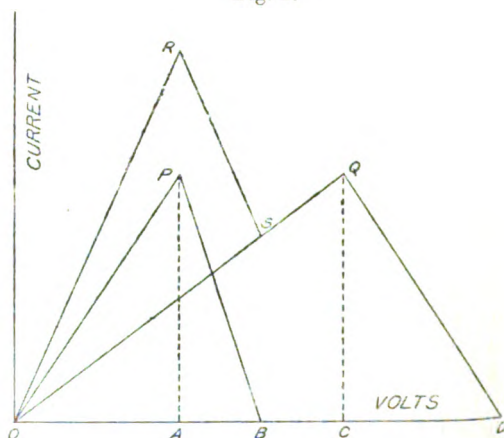


2800 mm. scale divs. per volt. The connexion was protected in the usual way by an earthed guard-ring. A condenser, the capacity of which varied in different experiments from  $\cdot 004$  to  $\cdot 007$  m.f., was connected in parallel with the electrometer. The insulated and the earthed electrodes were connected by an ebonite plug which left a gap of 2 mm. between them. The outer tube was in metallic connexion with tube D and with the sprayer and could be raised to any desired voltage.

*The Zeleny Double-Electrode Method.*

As the question at issue in these investigations depends upon the evidence for the existence of separate and distinct groups of ions given by the Zeleny method, it may be of advantage to consider briefly the theory of the method. The ionized air is drawn through a tube with two central electrodes separated by a short gap. The electrode nearer the entrance to the tube is earthed and the other electrode

Fig. 2.



is insulated and connected to an electrometer. The currents to the insulated electrode for various voltages applied to the outer tube are observed and a curve is plotted with the voltages as abscissæ and the current values as ordinates. If only one type of ion is present in the air and if the ionization is originally uniform over the cross-section of the tube, a curve of the type OPB shown in fig. 2 should be obtained. This is drawn for the case when the insulated electrode is half the length of the earthed electrode. As

the voltage is increased from zero to value OA the current increases uniformly. Saturation occurs for voltage OA, and AP represents the maximum current to the shorter electrode which is one-third the total saturation current. On further increasing the voltage, the current decreases uniformly and for voltage OB or  $\frac{2}{3}$  OA all the ions are captured on the earthed electrode. In practice, the curve OPB would be rounded off owing to diffusion of the ions, distortion of the electric field at the ends of the electrodes, etc. Curve OQD represents the curve due to an ion of one-half the mobility of the first ion and present in equal quantity, the saturation voltage OC being twice OA. To find the curve due to these two types of ions if present at the same time, the ordinates are added and curve ORSQD is obtained. Thus if two types of ions are present, a two-peaked curve should be found. Similar reasoning will apply to any number of classes of ions. A peak will represent a distinct type of ion, and the mobility of the ion can be calculated from the voltage corresponding to the peak from the formula

$$UV = \frac{Q \log_e \frac{b}{a}}{2\pi L},$$

where U = mobility,

V = critical voltage,

Q = volume of air passing per sec.

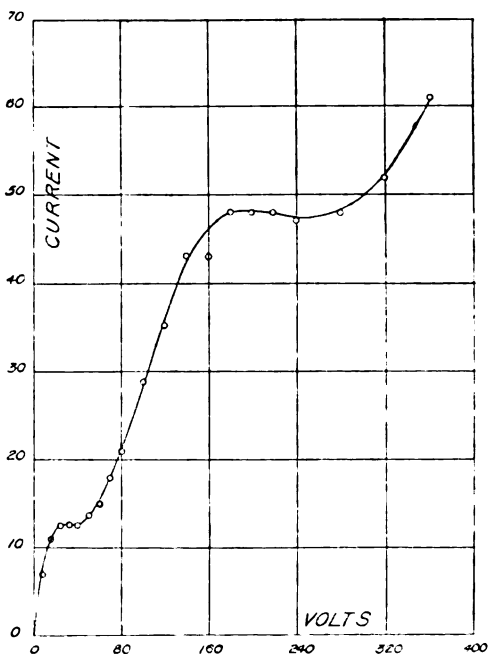
The character of the curve obtained in practice depends on the ratio of the lengths of the electrodes, on the ratio between successive mobilities, and on the number and relative quantities of the different classes present. The rounding-off of the curve for the various reasons cited may have the effect of obscuring some of the peaks. In curve ORSQD for example, observations may give the part of the curve SQ as a line parallel to the voltage axis, so that peak Q may not be well marked. A change in the mobilities of the ions as they pass along the tube will also tend to obscure the peaks, so that to get distinct evidence of separate groups, if they are present, it is necessary to reduce the time of the ions in the electric field as much as possible.

### *Results of Observations.*

Fig. 3 gives the result of an examination of ions the age of which was over 2 secs. when they entered the electric field. The time spent in the field was .14 sec. The current-

voltage curve refers to negative ions and was taken over the range 0-360 volts. It shows two discontinuities which represent peaks smoothed over in the fashions that have been suggested. The fact that the curve is rising at the higher voltages indicates that at least one other peak is present. When observations were further extended it was found, in fact, that the curve reached a maximum at about 650 volts and then descended. Now if the current-voltage relation is really of the kind shown in this curve, only one

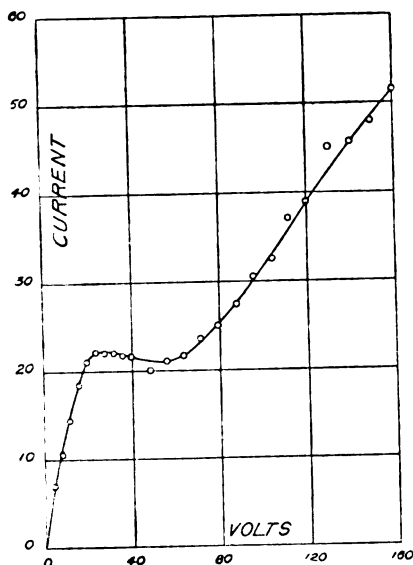
Fig. 3.



interpretation can be admitted, and that is that there are present at least three separate and distinct classes of ions. For if only one sharply defined class of ion is present, there should be one fairly sharp peak. On the other hand if, as Busse holds, the ions are of sizes which vary continuously over a fairly wide range, the curve should not only show a wide summit (the width being determined by the limits of the range) but should be smooth and convex throughout. The curve obtained is practically linear between the discontinuities and is a fair approximation to a portion of the

complete theoretical curve for a mixture of ions of different classes. It differs in shape from the curve given in fig. 2 because in that case only two kinds of ions were assumed to be present, and those in equal quantities. Here the first two classes which are disclosed are present in smaller quantities than the remaining group or groups, and the discontinuities appear in consequence on the left-hand side of the highest part of the curve. It is impossible that there could be any doubt as to the interpretation of a curve like that of fig. 3. The only question remaining, therefore, is whether the experimental evidence gives sufficient justification for drawing it as it has been drawn. This can be tested by working over the curve in closer detail.

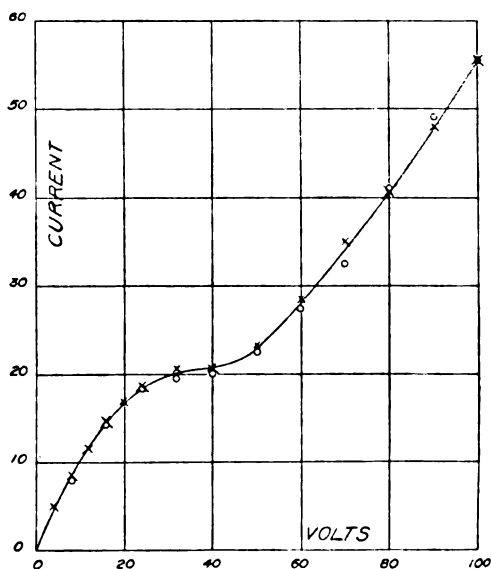
Fig. 4.



In fig. 4 is given the result of a close examination over the region 0-160 volts. This curve shows a peak at 28 volts corresponding to the first discontinuity in fig. 3. In general shape it corresponds very accurately with the theoretical Zeleny curve and discloses the existence of two distinct classes of ions. Thus the ascending parts are very nearly straight lines passing through the origin. In the earlier part of this paper the measures taken to secure steadiness were indicated. That they were successful is

shown by the accuracy with which observations could be repeated. Thus in fig. 5 two series of observations are plotted over the range 0-100 volts. One series was taken immediately after the other, and the close agreement between them shows how steady all the conditions were and disposes of the argument that fluctuations in the sprayer, in the air-current or in the field-voltage could account for the discontinuities. Moreover, it would be indeed strange if imperfections in the apparatus and irregularities in the method of working could occur in such a way as always to simulate a peak in the same part of the curve. It is not

Fig. 5.

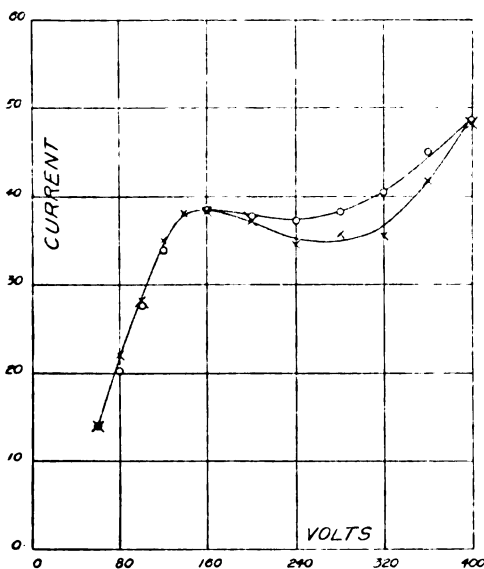


pretended that the apparatus used was perfectly adapted to secure the theoretical Zeleny curve. For example, small errors in the centring of the electrode no doubt existed. It would also be impossible under the conditions of experiment to secure absolute uniformity of the ionization over the cross-section of the tube. But the singularities shown on the curves could not arise out of such causes.

There is a real variation from day to day which affects not the existence of a peak but its degree of prominence. Thus the first peak is much more marked in fig. 4 than in fig. 3 or fig. 5. The same sort of variation is shown

in fig. 6 which shows the results of observations made on two successive days over the range 60–400 volts corresponding to the higher peak on fig. 3. The numbers plotted are, with six exceptions, the means of readings taken with ascending and descending voltages. While the day's interval has altered the shape of the curve, it has not obliterated the peak or altered its position. The mean value found in various curves for the position of this peak was 170 volts.

Fig. 6.



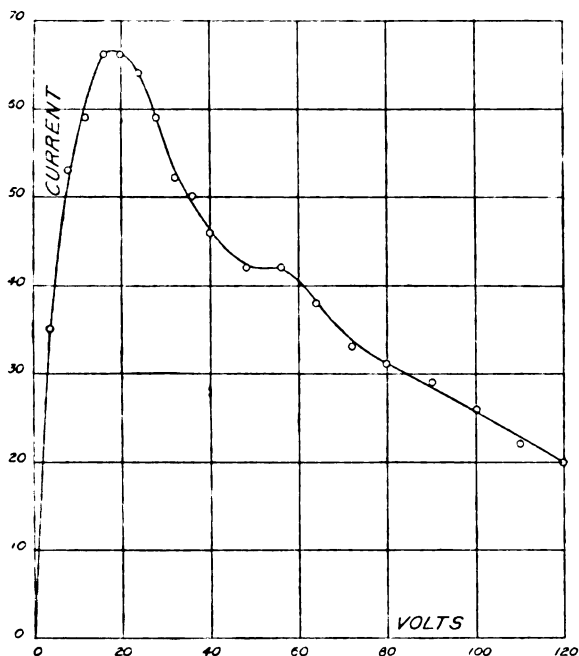
The curves obtained, of which those reproduced form a selection, enable us to fix with fair accuracy the positions of the two peaks at 30 volts and 170 volts. The next peak was found, as has been stated, at about 650 volts. The mobilities calculated from these critical voltages are  $\cdot 27$ ,  $\cdot 047$ , and  $\cdot 012$  cm./sec./volt/cm. These ions apparently correspond to the ions of mobilities  $\cdot 24$ ,  $\cdot 046$ , and  $\cdot 013$  observed by J. J. Nolan in his original examination of the ionization from a water-spray. He found also an ion of mobility  $\cdot 12$ , which is not disclosed in the curves that have been examined. In the ionization produced by bubbling air through mercury, groups of ions of mobilities  $\cdot 20$  and  $\cdot 048$  appear without any intermediate

group. It is possible that in the present work the non-appearance of the ion of mobility  $\cdot 12$  is due to some change in the conditions of experiment, *e.g.* to the use of a different type of sprayer. If this ion had appeared in the present experiments, it would have caused a peak in the current-voltage curve at 67 volts and thus would have filled up the marked concavity in the curve. In fact it is to the non-appearance of such a peak that the curves reproduced owe their convincing character. The change in the forms of the peaks from day to day may be ascribed to the presence of this or other ions in small and varying quantities.

The results so far given support in the fullest fashion the conclusions previously advanced as to the character of the ionization and, as far as they go, are in numerical agreement with the previous results. Nothing more than this was contemplated in the present work, for to cover the whole ground once more and to work over all the types of ions previously found would involve a very extensive series of observations the necessity for which has not been shown.

Reference was made earlier in this paper to the fact that different results were obtained using different types of sprayer. The difference was not in the essential character of the ionization, but in the way in which the groups occurred. To illustrate this point an example is given in fig. 7 of a curve obtained with a sprayer differing from that used in the work already dealt with. This curve shows a well-marked peak at 18 volts and indications of a peak at 55 volts. The mobilities corresponding to the voltages are  $\cdot 36$  and  $\cdot 12$  (the air-current also differed in this case). The general shape of the curve so far as it has been plotted is due to the fact that the ion of mobility  $\cdot 36$  is present in considerable quantity. The ion of mobility  $\cdot 27$  which was so prominent in the previous cases does not appear here, whereas there are indications of the presence of the ion of mobility  $\cdot 12$  previously missing. The ion of mobility  $\cdot 36$  probably corresponds to that of mobility  $\cdot 32$  or  $\cdot 31$  found with mercury and alcohol. Possibly we have in this curve an explanation of Busse's failure to detect separate groups of ions. Under certain conditions of experiment the groups might occur in such relative quantities that the current-voltage curve resulting would with difficulty be distinguished from a smooth curve. For example, a long and careful working over the curve in fig. 7 would be necessary to prove conclusively the existence of a discontinuity at 55 volts.

Fig. 7.



### Conclusions.

It has been shown that when water is sprayed, the ions produced assume preferentially certain definite sizes. Whether they are exclusively of these sizes or whether there is in addition a general background of ionization covering all sizes, our experiments are not critical enough to detect. But combining the present work with that previously reported, it is clear that by a variety of processes a series of groups of ions can be produced, the same ions tending to appear whatever the origin of the ionization. Some of the complexity of the ionization might be explained by assuming the existence of multiple charges on some of the ions, but a study of the mobility values will show that very little simplification can be achieved in this way. We must assume that the ions are of many different stable or semi-stable sizes. Reasons have been given for believing that the ions are composed of water \*. The results then suggest that there must be a variety of water aggregates

\* J. J. Nolan, Proc. Roy. Soc. A. xciv. p. 112 (1917).



each enjoying a certain degree of stability. J. J. Thomson\* and Langevin† have shown theoretically the possibility of the existence of a water-spherule of a certain size which would be stable even in dry air. The existence of this complex ionization suggests that there must be several such stable sizes.

It may be remembered in this connexion that in addition to the "small" ions and the Langevin or "large" ions found in atmospheric air, Pollock‡ has found an ion of mobility .02 in dry air in Sydney. Dorno§ found at Davos ions of mobility .04, and Knoche|| over the Pacific ions of mobility .05. While Pollock's ion does not fit readily into our scheme, the ions found by Dorno and Knoche may very well correspond with the ion of mobility .047 which is disclosed in the present work and which was prominent in the previous experiments. It is possible even that the whole series of ions exist to some degree in atmospheric air. The problem presented by these ions is a problem in the physics of small aggregates of water. That they are charged is an accident due to their method of production, due for example in the spraying and bubbling of liquids to the fact that rupture of electrical double layers occurs. But the sizes of the ions tell us nothing about the constitution of these double layers, any more than the ions of identical sizes produced from phosphorus tell us anything about the manner of their production.

XXXIV. *Measurement of the Resistance of a Condenser at Radio Frequency.* By CHARLES D. CALLIS, Assistant in Physics, Indiana University, U.S.A.¶

IT appears that the resistance of a condenser has not been measured at radio frequencies. All measurement of the losses of a condenser at radio frequency has been made by comparative methods. It is customary to measure the resistance of a standard condenser at low frequency (one or two thousand cycles) and, if the resistance is low or negligible, to consider the resistance at high frequency to be zero. This is based on the fact that dielectric losses diminish

\* 'Conduction of Electricity through Gases,' p. 149 (1903).

† See Chauveau, *Le Radium*, March-April, 1912.

‡ Pollock, *Le Radium*, p. 129 (1909). *Phil. Mag.* xxix. p. 636 (1915).

§ C. Dorno, *Licht und Luft im Hochgebirge*, Braunschweig, 1911.

|| W. Knoche, *Phys. Zeitschrift*, xiii. p. 322 (1912).

¶ Communicated by Professor R. R. Ramsey.

with frequency \*. The resistance of a given condenser is compared with a standard by placing the condenser in a high-frequency circuit and measuring the resistance of the circuit, and then replacing the condenser with the standard and measuring the resistance of the circuit again, the difference in the two results being due to the difference of resistance of the two condensers. Since the resistance of the standard is assumed to be zero, the difference is the resistance of the condenser.

The investigation, of which this article is a report, is the result of a method devised by Professor R. R. Ramsey, of Indiana University, and worked out under his direction by the writer. It is an attempt to make absolute measurements of the resistance of a variable condenser at a frequency of one million cycles per second.

The method of measuring radio frequency resistance of a circuit is very simple. A radio frequency galvanometer or milliammeter is placed in the circuit of a coil and a condenser. This circuit is tuned so as to be in exact resonance with an oscillating circuit and the current noted in the meter. A known resistance is inserted and the current noted again. From these readings the resistance of the circuit is determined. A particular case is the half-deflexion method, in which resistance is inserted until the current is reduced to half the original value and then the resistance of the circuit is equal to that of the resistance inserted. The resistance as measured is that of the coil, of the condenser, and of the meter. The meter is usually so constructed that its resistance is the same as the D.C. resistance. The problem is to separate the resistance of the condenser from that of the coil.

It is well known that the resistance of a straight wire is larger for alternating current than for direct current, due to the skin effect. It is also known that the high-frequency resistance of a wire is different when it is coiled from that when it is straight and far removed from other wires. The impedance of a coil at high frequency is so great that it is practically impossible to force an appreciable amount of current through the coil without placing it in connexion with a condenser and tuning the circuit. The measurement of the resistance of the coil without the condenser is out of the question.

The method used in this investigation is to wind two coils as nearly alike as possible. Coil No. 1 is placed in series

\* Bureau of Standards, Bulletin 74, pp. 113, 126, 190. Louise McDowell, *Phys. Rev.* xxiii. p. 507 (1924).

with the condenser and meter and tuned to the same frequency as that of the generator, and the resistance of the circuit measured by the method described above. Coil No. 2 is then inserted, and since it is nearly the same as No. 1 the setting of the variable condenser is approximately the same as in the first case. The resistance of this circuit is then measured.

Adding the two results gives the equation :

$$R_1 + R_2 = r_1 + r_2 + 2C + 2m. \quad (1)$$

$R_1$  and  $R_2$  are the two measured resistances,  $r_1$  and  $r_2$  are the resistances of the coils,  $C$  the resistance of the condenser, and  $m$  is the resistance of the milliammeter. The two coils are then placed in series opposition in the circuit with the condenser and milliammeter, and their positions adjusted so that the combined inductance of the two is equal to the inductance of one coil. The circuit is then in resonance with the generator with the condenser set at the same capacity. Then the resistance  $R_3$  of the circuit is measured.

$$R_3 = r_1 + r_2 + C + m. \quad (2)$$

Subtract equation (2) from equation (1) we get

$$(R_1 + R_2) - R_3 = C + m. \quad (3)$$

Since  $m$  is known, the value of the resistance of the condenser at a particular setting has been determined. This is true provided the resistances of the two coils placed in series opposition is the sum of the separate values. From the above readings it is possible to determine the resistances of the coils as well as the resistance of the condenser. Preliminary measurements were made with coils of No. 20 copper wire. These measurements suggested making the coils of fine wire. Coils were then constructed of No. 36 copper wire, the A.C. resistance of which, according to tables already compiled, is not more than .6 per cent. greater for one thousand kilocycles than for direct current. Checking through with coils made of this wire and solving for the resistance of the coils we get a result which, within the accuracy of the apparatus, is the same as the D.C. resistance of the coils. Therefore the assumption is made that changing the relative position of coils made of No. 36 or No. 40 wire does not change the resistance of the coils, and the value obtained for the condenser is the true resistance of the condenser. Nine pairs of coils were made with this fine wire. The number of turns was adjusted to give readings at various points on the condenser scale.

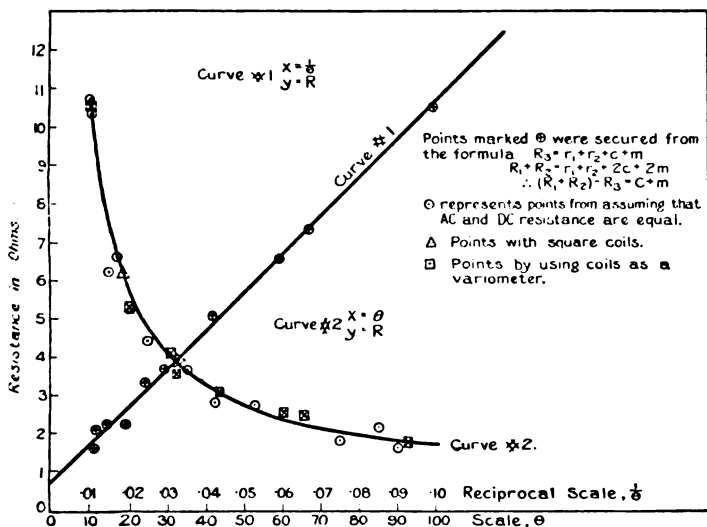
The condenser used was a commercial forty-one plate

variable air-condenser with semicircular plates of the "low loss" type. In this condenser the capacity is directly proportional to the dial readings, the maximum capacity being 0.001 microfarad. The resistance of the condenser was found to vary inversely with the capacity.

The resistance as found with the nine sets of coils and the reciprocal of the dial readings are plotted in the figure giving the straight line, Curve No. 1. Curve No. 2, which is an equilateral hyperbola, is plotted from data taken from the straight line. The equation of the straight line is

$$R = 0.75 + \frac{99}{\theta},$$

where  $\theta$  is the scale-reading at any particular setting.



Since the calculated value of the resistance of the coils was approximately the same as that of the D.C. resistance, other measurements were made with single coils of No. 36 wire, the resistance of which was assumed to be the measured D.C. resistance. The values of the resistance of the condenser are shown on the curve by the circled points. Coils made of No. 40 wire were used in the same manner, and the values of the resistances indicated in the same way. Measurements were also made with two coils in series, and their relative positions changed so as to change the inductance and thus get several settings of the condenser. The values of these resistances are indicated on Curve No. 2 by crossed squares.

The coils were made in the Lorentz form in which the wire is interwoven on pegs set in a circle, tied with cotton cord, and then removed from the forms. The coils were then self-supporting without a core. Since all the coils have been wound after the same pattern, it was thought that there might be danger of a systematic error due to the form of the coil. Coils were wound on wooden cross-arms, making square coils about 50 centimetres on a side. The turns in these coils were placed 1 centimetre apart. Measurements of the resistance of the condenser using these coils are shown on Curve 2 by points in triangles.

It will be noted that all these points follow the equilateral hyperbola, showing that all results are the measurement of the resistance of the condenser, and not some change in resistance of the coils due to placing wire in the field caused by a current in other wires.

The points do not lie on the curve exactly. This is due to the fact that the absolute error made in measuring the total resistance of the circuit appears with the value of the condenser resistance. The total resistance of the circuits varied from 10 ohms for large capacity to 75 ohms for small capacity.

The oscillator was a 5-watt tube, with a 350 volt D.C. generator for plate supply. This generator was run by a motor on the regular University circuit. Any variation on the line caused a variation of the plate voltage and a variation of the output of the tube. These variations introduced large errors in the measurements. It is hoped to procure a more powerful oscillator and a constant potential plate supply and make more refined measurements of the resistance of a condenser.

The purpose of this article is to give a method by which the resistance of a variable air-condenser can be measured. The resistance is a measurable quantity, and the resistance of a "low loss" condenser is not small or zero as has been assumed by those who base their assumptions on dielectric measurements. This particular condenser has a resistance which varies from about 1.7 ohms to 15 ohms. If this high value is not true the only other assumption that can be made is, that given any number of coils made of the same size wire (No. 40) wound in any form whatever; various diameters, number of turns, and spacings; but wound so as to have the same inductance, then the difference between the A.C. resistance and the D.C. resistance is the same constant value for each coil.

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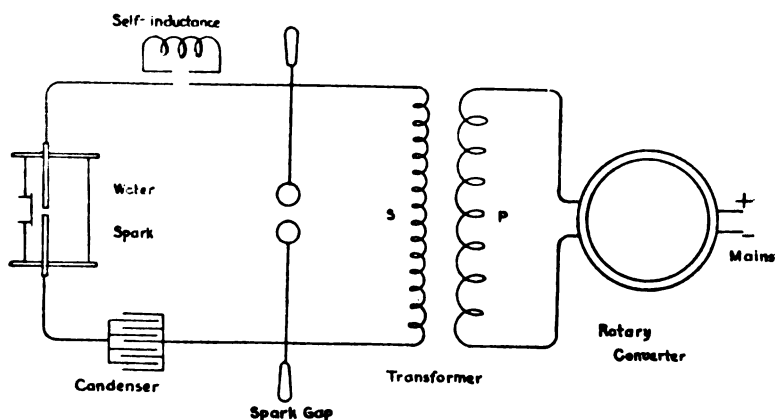
XXXV. *On the Water-Spark Absorption Spectrum of Iron.*  
By N. K. SUR, M.Sc. (Physics Department, Allahabad University) \*.

[Plate VII.]

IT has long been known that when a spark is produced between two metal electrodes immersed in distilled water, it emits a fairly continuous light which is under certain conditions traversed by absorption lines of the metal of the electrode. The spectrum of the spark under water has been studied by Wilsing, Hale, Konen †, and in recent years by Victor Henri ‡ and his students, Hulburt §, and Angerer and Joos ||.

The present investigation arose out of an attempt to see whether the water-spark spectrum can be used as a source

Fig. 1.



ARRANGEMENT FOR WATER SPARK.

of continuous ultra-violet light in place of other sources, *e.g.* the positive crater of the arc, or a tungsten lamp with quartz windows. As a result of these studies many new facts have been brought to light, and it has been found that

\* Communicated by Professor M. N. Saha.

† Konen, *Ann. der Physik*, vol. ix. p. 779 (1902).

‡ Victor Henri, *Proc. Roy. Soc. London, A*, vol. cv. pp. 668-69 (1924)

§ Hulburt, *Phys. Review*, vol. xxiv. pp. 129-33 (1924).

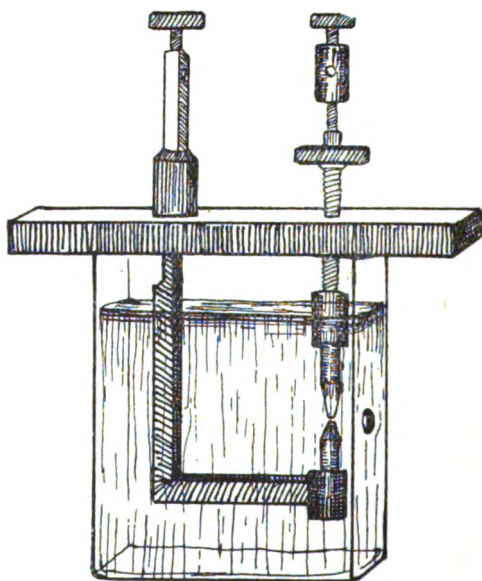
|| Angerer & Joos, *Ann. der Physik*, vol. lxxiv. pp. 746-47 (1924).

the arrangement is very suitable for studying the absorption spectra of elements.

The apparatus employed is shown in figs. 1 and 1 *a*.

*Transformer.*—As shown in the diagram, the spark is produced under water by a high-frequency discharge from a high-tension transformer. T is a high-tension transformer of  $\frac{1}{4}$  KW capacity. The primary of the transformer is furnished with alternating current from a rotary converter working at 110 volt D. C. The secondary furnishes an alternating e.m.f. of 15,000–20,000 volts, and works very smoothly.

Fig. 1 *a*.



Sparking vessel

*Condenser.*—As the leyden-jars are frequently punctured, we constructed a condenser after Millikan's pattern. This consisted of thick ( $\frac{1}{2}$  cm.) window glasses  $34 \times 23$  cm. with alternate sheets of zinc. The whole was placed under oil, in a porcelain tank. The advantage is that the capacity can be varied with the least amount of trouble within very wide limits, and if any plate is punctured, it can be immediately replaced.

It may be mentioned here that the potential to which the condensers can be charged depends on the rate of power-supply, as was first pointed out by Anderson \*. It is no use trying condensers of large capacity unless the rate of power-supply is proportionately larger. When the given source of high tension has a definite rate of power-supply, there is a certain definite value of the capacity with which the apparatus works best.

*The Sparking Vessel.*—In the experiments of Victor Henri and Angerer and Joos a teak-wood vessel was used. This type of vessel was first tried, but as the sides were cemented by shellac and other adhesives, they leaked very badly. It was found that an ordinary glass cell was quite good for the purpose. A hole was drilled on one side which was stopped by means of a quartz window. The sparking pieces were carried by an ebonite lid, and were provided with sockets, into which rods of any metal could be inserted and fixed with a screw. The distance between the metallic pieces could be adjusted by screw-heads fixed to the ebonite lid. After sparking for some time the water gets dirty and cuts off the ultra-violet light. The water could be siphoned off through a hole at the top and fresh distilled water put in.

*Working of the Apparatus.*—It will be seen from the diagram that the discharge takes place in a high-frequency oscillatory circuit completed through the condenser, the water-spark, and the parallel spark-gap. The frequency of oscillation could be varied by inserting different self-inductances in the circuit. The nature of the spectrum emitted can, by this means, be varied within wide limits, as was found by Stücklen †. This point is the subject of a separate investigation by Mr. P. K. Kichlu, and will be published later. It has been found that if more self-inductances are inserted, the discharge emits, instead of a strong continuous spectrum crossed with absorption lines, a less continuous spectrum with superposed emission lines. In the present experiments the self-induction was cut down to the minimum value.

Mr. Kichlu has found that the geometrical form of the rods has a marked influence on the nature of the spectrum. Sharp-pointed electrodes always give emission lines. Flat electrodes gave a strong continuous spectrum with absorption lines. The spark was generally 3 to 4 mm. in length and 2 to 3 mm. in breadth, and emitted an intense bluish-white light.

\* Anderson, *Astrophys. Journal*, vol. lix. pp. 76-96 (1923).

† Stücklen, *Zeits. für Physik*, vol. xxx. pp. 24-39 (1924).



*Theory of the Water-Spark.*

Victor Henri\* has formulated a theory of the water-spark. According to him the aureole of light consists of an inner core composed of highly-ionized metallic vapour, surrounded by a cooler mantle of vapour. The inner vapour space emits a continuous spectrum, and the absorption lines are produced in the outer mantle of cooler vapour when it is traversed by the continuous light.

Besides the metallic lines, prominent absorption lines are obtained on all plates at about  $\lambda = 3100$  Å.U. They have been ascribed to (OH) ions.

That very high pressure is developed inside the spark is at once apparent. After the spark has passed for some time, the electrodes appear as if their heads have been battered by a hammer. If the lower screw is not tight enough, the electrode is pressed downwards. The water in the vessel is in a violent state of agitation, and sometimes the quartz window breaks under pressure. It is possible to measure the pressure developed, but this has not been attempted as yet.

According to the theories of Eddington† and Saha‡, a typical star consists of a core of highly-ionized gas with an outer layer of cooler vapour containing neutral as well as ionized atoms. The water-spark is thus a miniature star, and if water could be replaced by some transparent compressed gas, like  $H_2$  or He, probably the continuous spectrum could be extended by a substantial amount to the ultra-violet. With the present arrangement we have obtained the spectrum down to  $\lambda = 2100$  Å.U. on Seed 40 plates. The times of exposure varied from 1 to 5 minutes in the region  $\lambda = 3000$  Å.U.

This arrangement is considered to be a substantial improvement on that of Victor Henri and his co-workers, because they had to expose their plates from 3 to 45 minutes, while we have found generally 1 minute to be quite sufficient. We used a 5-foot concave grating with a ruled surface of  $1\frac{1}{2}$  inches and giving a dispersion of 11.11 Å.U. per mm. in the first-order spectrum. Victor Henri used a quartz spectrograph which has more light-gathering power than our grating. I am now engaged in making a systematic study of the absorption spectra of elements with this

\* Victor Henri, *cide* Stücklen's paper cited above.

† Eddington, *Month. Not. Roy. Astro. Soc.* vol. lxxxiii. p. 32 (1923); and *Zeits. für Physik*, vol. vii. p. 351 (1921).

‡ Saha, "On a Physical Theory of Stellar Spectra," *Proc. Roy. Soc. A*, vol. ci. pp. 138-153 (1921).

apparatus. The first element studied was iron, and the results are reported below. A portion of the iron spectrum at about  $\lambda=4000$  Å.U. photographed in the third-order spectrum is reproduced (see Pl. VII.).

### Absorption Spectrum of Iron.

The lines which have been obtained in the water-spark as absorption lines are given in Table I. The wave-lengths are taken from the measurements of Burns \*, rounded off to two places of decimals; intensity and temperature class from King †; and series classification from the recent work of Laporte ‡. Many weak lines, which are not to be found in Laporte's list, have been obtained in absorption.

TABLE I.

Iron lines obtained in water-spark as absorption lines.

Wave-lengths (Burns).	Wave-numbers (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
4071.75	24552.57	40 II	$\bar{F}_2^1 - F_2^1$	
4063.60	24601.78	45 II	$\bar{F}_3^1 - F_3^1$	
4045.82	24709.91	60r II	$\bar{F}_4^1 - F_4^1$	
3930.30	25436.14	25R I	$d_2^1 - \bar{d}_3^1$	
3927.93	25451.45	30R I	$d_1^1 - \bar{d}_2^1$	
3922.92	25484.03	25R I	$d_3^1 - \bar{d}_4^1$	
3920.26	25501.31	20r I	$d_0^1 - \bar{d}_1^1$	
3902.95	25614.41	20 II	$\bar{F}_3^1 - \bar{D}_3^1$	
3899.71	25635.67	30R I	$d_2^1 - \bar{d}_2^1$	
3898.01	25646.86	10 II	$\bar{f}_1^1 - \bar{d}_2^2$	
3895.66	25662.35	25r	$d_1^1 - \bar{d}_0^1$	
3887.05	25719.16	15 I	$\bar{f}_4^1 - \bar{d}_4^2$	
3886.29	25724.24	40R I	$d_3^1 - \bar{d}_3^1$	
3878.58	25775.35	100R II	$d_2^1 - \bar{d}_1^1$	
3878.02	25779.05	60R II	$\bar{f}_3^1 - \bar{d}_3^2$	
3872.51	25815.77	60R II	$\bar{f}_2^1 - \bar{d}_2^2$	

\* Burns, *vide* Kayser-Konen, *Handbuch der Spectroskopie*, vol. vii.

† King, *Astrophys. Journ.* vol. xxxvii. p. 239 (1913), and vol. lv. p. 318 (1922).

‡ Laporte, *Zeits. für Physik*, vol. xxiii. p. 135 (1924), and vol. xxvi. p. 1 (1924).

TABLE I. (continued).

Wave-lengths (Burns).	Wave-numbers (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
3865.53	25862.38	40r II	$f_1^1 - \bar{d}_1^2$	Breaks the selection-principle.
3859.91	25900.00	300R I	$d_4^1 - \bar{d}_4^1$	
3856.37	25923.77	100R IA	$d_3^1 - \bar{d}_3^1$	
3850.82	25961.16	15r II	$\bar{f}_2^1 - \bar{P}_2^1$	
3841.05	26027.17	80r II	$\bar{F}_2^1 - \bar{D}_1^1$	
3834.23	26073.50	80R II	$\bar{f}_3^1 - \bar{d}_2^2$	
3827.83	26117.10	75r II	$\bar{F}_3^1 - \bar{D}_2^1$	
3825.89	26130.35	125R II	$\bar{f}_4^1 - \bar{d}_3^2$	
3824.44	26140.19	100R IA	$d_4^1 - \bar{d}_3^1$	
3820.43	26167.66	200R II	$\bar{f}_5^1 - \bar{d}_4^2$	
3815.84	26199.11	100r II	$\bar{F}_4^1 - \bar{D}_3^1$	Not clearly resolved.
3767.19	26537.43	60R II	$f_1^1 - f_1^2$	
3763.59	26561.42	80R II	$\bar{f}_2^1 - f_2^2$	
3758.23	26600.71	125R II	$\bar{f}_3^1 - f_3^2$	
3749.49	26662.76	125R II	$\bar{f}_4^1 - f_4^2$	
3748.26	26671.45	125R IA	$d_1^1 - f_2^1$	
3745.90	26688.31	80R IA	$d_0^1 - f_1^1$	
3745.56	26690.69	150R I	$d_2^1 - f_3^1$	
3743.36	26706.35	40R IIA	$\bar{f}_2^1 - f_2^2$	
3737.14	26750.88	200R I	$d_3^1 - f_4^1$	
3734.87	26767.12	150R II	$\bar{f}_5^1 - f_5^2$	
3733.32	26778.22	80R IA	$d_1^1 - f_1^1$	
3727.62	26819.15	40R II	$\bar{f}_3^1 - f_2^2$	
3722.57	26855.57	100R I	$d_2^1 - f_2^1$	
3719.94	26874.53	300R I	$d_4^1 - f_5^1$	
3709.25	26952.00	40R II	$\bar{f}_4^1 - f_3^2$	
3606.68	27718.45	20 III		
3586.99	27879.61	30 II	$f_2^1 - \bar{g}_2^1$	
3583.32	27899.14	2 IV		
3581.20	27915.62	250R I	$\bar{f}_5^1 - \bar{g}_5^1$	
3573.84	27973.15	4 IV		Not resolved.
3573.40	27976.59	2 IV		
3570.24	28001.36	20 III	.....	
3570.10	28002.43	100R I	$\bar{f}_4^1 - \bar{G}$	

TABLE I. (continued).

Wave-lengths (Burns).	Wave-numbers (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
3565.38	28039.50	60r II	$\bar{f}_3^1 - \bar{G}_4^1$	
3560.71	28076.30	5 IV		
3547.20	28183.22	? ?		
3500.57	28558.63	2 IV		
3497.84	28580.9	40 I	$d_1^1 - p_2^1$	
3490.58	28640.3	100r I	$d_3^1 - p_3^1$	
3476.71	28754.6	40 I	$d_0^1 - p_1^1$	
3475.45	28765.1	70r I	$d_2^1 - p_2^1$	
3465.86	28844.6	60r I	$d_1^1 - p_1^1$	
3443.88	29028.8	50r I	$d_2^1 - p_1^1$	
3440.99	29053.2	75R I	$d_3^1 - p_2^1$	Not clearly resolved.
3440.61	29056.3	150R I	$d_4^1 - p_3^1$	
3427.13	29170.60	20 III	.....	Not resolved. Breaks the selection-principle.
3426.99	29171.76	2 IIIA	$f_2^1 - p_2^2$	
3407.47	29338.91	20 III		Breaks the selection-principle.
3401.52	29390.18	6 III	$f_4^1 - p_3^2$	
3399.34	29409.06	15 III		
3222.07	31027.03	20 III		
3182.99	31407.95	3 IV		
3119.50	32047.16	6 IV		
3100.67	32241.78	20 II	$\bar{f}_3^1 - \bar{d}_3^3$	Not clearly resolved.
3100.31	32245.56	20 II	$\bar{f}_2^1 - \bar{d}_2^3$	
3099.97	32249.05	15 II	$\bar{f}_4^1 - \bar{d}_4^3$	Not resolved.
3099.90	32249.79	20 II	$\bar{f}_1^1 - \bar{d}_1^3$	
3083.75	32418.71	20 II	$\bar{f}_2^1 - \bar{d}_1^3$	
3075.73	32503.25	25r II	$\bar{f}_3^1 - \bar{d}_2^3$	
3067.25	32593.04	30r II	$\bar{f}_4^1 - \bar{d}_3^3$	
3059.09	32679.98	100R I	$d_3^1 - \bar{d}_4^2$	
3057.45	32697.50	40R II	$f_5^1 - \bar{d}_4^3$	
3047.61	32803.10	100R I	$d_2^1 - \bar{d}_3^2$	
3037.39	32913.43	80R I	$d_1^1 - \bar{d}_2^2$	
3025.85	33039.01	50R I	$d_0^1 - \bar{d}_1^2$	
3024.04	33058.78	15r IA	$d_1^1 - p_2^1$	
3021.08	33091.17	150R I	$d_3^1 - \bar{d}_3^2$	
3020.64	33095.93	200R I	$d_4^1 - \bar{d}_4^2$	Not resolved; comes as a broad line.
3020.50	33097.53	100R II	$d_2^1 - \bar{d}_3^2$	

TABLE I. (*continued*).

Wave-lengths (Burns).	Wave-number (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
3017.63	33128.96	15r 1A	$d_1^1 - d_1^2$	Not sure.
3008.14	33233.45	60R I	$d_1^1 - d_0^2$	
3000.96	33313.08	100R I	$d_2^1 - d_1^2$	
2999.52	33329.02	30R II	$f_5^1 - f_5^2$	
2994.50	33384.84	100R ? I	$d_0^1 - P_1^1$	
2994.43	33385.54	100R I	$d_3^1 - d_2^2$	Not resolved; comes as a broad line
2983.57	33507.13	125R I	$d_4^1 - d_3^2$	
2981.45	33531.00	20r I	$d_3^1 - P_2^1$	
2973.14	33624.72	60R I	$d_2^1 - f_3^2$	
2973.24	33623.60	60R I	$d_3^1 - f_4^2$	
2970.11	33659.02	40R I	$d_1^1 - f_2^2$	Break the selection- principle analogous to the absorption of 1S - <i>md</i> lines of alkalies as shown by Datta, Proc. Roy. Soc. Lond. A, ci. p. 545 (1922).
2966.90	33695.37	125R II	$d_4^1 - f_5^2$	
2965.26	33714.06	20 II	$d_0^1 - f_1^2$	
2957.37	33803.97	30R II	$d_1^1 - f_1^2$	
2953.94	33843.18	50R II	$d_2^1 - f_2^2$	
2950.25	33885.55	20r IV		
2947.88	33912.84	60R I	$d_3^1 - f_3^2$	
2936.90	34039.53	60R I	$d_4^1 - f_4^2$	
2929.01	34131.31	25r I	$d_3^1 - f_2^2$	
2912.16	34328.72	20r I	$d_4^1 - f_3^2$	
2874.18	34782.36	10	$d_4^1 - f_5^1$	
2869.31	34841.38	10 I	$d_3^1 - g_4^1$	
2851.80	35055.30	15r II	$f_1^1 - g_2^2$	
2843.97	35151.81	20r II	$f_2^1 - g_3^2$	
2838.12	35224.26	10 III	$f_2^1 - g_2^2$	
2832.43	35295.02	25r II	$f_3^1 - g_4^2$	
2828.81	35340.18	7 III		Breaks the selection- principle.
2825.69	35379.19	6 II	$d_4^1 - G_5^1$	
2823.28	35409.40	20 II	$f_3^1 - g_3^2$	? (Laporte).
2813.29	35535.13	30R II	$f_4^1 - g_5^2$	
2807.24	35611.72	2 III	$d_4^1 - g_3^1$	Breaks the selection- principle.

TABLE I. (continued).

Wave-lengths (Burns).	Wave-numbers (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
2806.99	35614.88	20 II	.....	Doubtful.
2804.52	35646.25	20 II	$\bar{f}_4^1 - \bar{g}_4^2$	? (Laporte).
2797.78	35731.34	15 III	.....	
2795.55	35760.62	.....	$\bar{f}_4^1 - \bar{g}_3^2$	? (Laporte).
2795.01	35767.53	3 III	$d_4^1 - \bar{G}_4^1$ }	Breaks the selection-principle.
2788.11	35856.04	30 II	.....	Not resolved.
2787.94	35858.02	5 II	.....	
2778.23	35983.55	20 III	$\bar{f}_6^1 - \bar{g}_6^2$	? (Laporte).
2778.08	35985.49	3 III		
2772.08	36063.37	20 II	$d_2^1 - p_3^2$	Laporte gives the neighbouring line 2772.11 (int. 1) as $d_2^1 - p_3^2$ , but this is evidently wrong.
2763.11	36180.44	4 III		
2761.79	36197.73	18 III		
2756.33	36269.38	20 I	$d_1^1 - p_2^2$ }	Not resolved.
2756.27	36270.23	3 ?	$d_3^1 - F_4^1$ }	
2753.69	36304.20	3 III		
2750.15	36351.00	25r II	$d_3^1 - p_3^2$	
2746.99	36392.74	20 III		
2744.53	36425.36	8 III	.....	Not clearly resolved.
2744.07	36431.44	10 II	$d_0^1 - p_1^2$ }	
2742.41	36453.53	30r II	$d_2^1 - p_2^2$	
2739.55	36491.56	? ?		
2737.31	36521.39	20r II	$d_1^1 - p_1^2$	
2735.48	36545.86	8 III		
2733.58	36571.26	15 II		
2730.98	36606.08	2 III		
2728.97	36633.03	2 ?	$d_1^1 - F_2^1$ }	Not resolved.
2728.83	36634.92	2 III	.....	
2728.03	36645.66	3 III	.....	
2723.58	36705.50	15 II	$d_2^1 - p_1^2$	
2720.91	36741.55	40r II	$d_3^1 - p_2^2$	
2719.04	36766.84	60R II	$d_4^1 - p_3^2$	

TABLE I. (continued).

Wave-lengths (Burns).	Wave-numbers (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
2717.79	36783.72	2 III		
2711.66	36866.87	4 III		
2704.00	36971.30	? ?		
2690.07	37162.66	2 III	$d_4^1 - F_3^1$	} Not resolved.
2689.84	37165.92	2 III	.....	
2684.86	37234.85	? ?	.....	
2684.76	37236.23	? ?	.....	
2681.59	37279.63	? ?		
2669.50	37448.76	2 IV		
2651.72	37700.17	2 III		
2647.57	37759.26	3 III	$d_3^1 - D_3^1$	
2641.65	37843.86	4 III		
2635.82	37927.57	8 III		
2632.60	37973.89	2 IIIA	$d_2^1 - \bar{D}_2^1$	
2629.60	38017.28	2 III	$d_0^1 - D_1^1$	
2628.30	38036.08	? ?		
2623.54	38105.08	5 III		
2623.38	38107.43	2 III	$d_1^1 - \bar{D}_1^1$	
2618.72	38175.22	2 III	$d_4^1 - \bar{D}_3^1$	
2618.03	38185.27	5 III		
2615.43	38223.23	? ?		
2613.84	38246.48	? ?		
2611.89	38275.04	? ?		
2606.84	38349.17	6 III		
2599.58	38456.27	6 III	.....	} Not resolved.
2599.41	38458.79	? ?	.....	
2598.38	38474.03	? ?		
2593.53	38546.97	? ?		
2588.01	38628.19	8 III		
2585.89	38659.86	20 IV		
2584.54	38680.04	8 III		
2577.93	38779.21	? ?		
2576.70	38797.72	4 III		
2575.76	38811.67	? ?		
2574.37	38832.83	? ?		

TABLE I. (continued).

Wave-lengths (Burns).	Wave-number (vacuum).	Intensity & temperature class King).	Series- notation (Laporte).	Remarks.
2570.86	38885.85	? ?	.....	Not resolved.
2570.54	38890.68	? ?	.....	
2566.92	38945.52	? ?		
2563.49	38997.64	? ?		
2562.54	39012.09	? ?		
2549.62	39209.92	10r III	$d_3^1 - d_4^3$	Not clearly resolved.
2545.98	39265.71	10r III	$d_2^1 - d_3^3$	
2540.98	39343.20	10R III	$d_1^1 - d_2^3$	
2535.61	39426.34	8r III	$d_0^1 - d_1^3$	
2527.44	39553.82	15r II	$d_3^1 - d_3^3$	
2522.86	39625.63	40R II	$d_4^1 - d_4^3$	
2518.11	39700.36	12r II	$d_2^1 - d_1^3$	
2512.37	39791.08	5r III	$d_3^1 - d_1^3$	
2510.84	39815.25	15R II	$d_3^1 - d_2^3$	
2501.14	39969.72	20R II	$d_4^1 - d_3^3$	
2491.16	40129.79	20R II	$d_1^1 - f_2^3$	
2490.66	40137.91	30R II	$d_2^1 - f_3^3$	
2489.76	40152.42	15r II	$d_0^1 - f_1^3$	
2488.15	40178.41	40R II	$d_3^1 - f_4^3$	
2484.18	40242.45	15R II	$d_1^1 - f_1^3$	
2483.54	40252.95	10 II	.....	
2483.28	40257.21	60R II	$d_4^1 - f_5^3$	
2479.78	40313.95	20R II	$d_2^1 - f_2^3$	
2479.48	40318.86	6 III	.....	
2472.91	40425.46	12R II	$d_3^1 - f_3^3$	
2472.88	40426.53	? ?	$d_2^1 - f_1^3$	Doubtful.
2465.16	40553.04	6 III		Doubtful.
2462.65	40594.35	10r II	$d_4^1 - f_4^3$	
2462.19	40601.94	4 III	$d_3^1 - f_2^3$	
2453.48	40746.10	5 III		
2447.72	40842.01	4 II ?	$d_4^1 - f_3^3$	
2438.19	41001.59	2 III		

The group  $d^1 - f^3$  (multiplet 8) has been obtained in absorption by Gieseler and Grotrian (*Zeits. für Physik*, vol. xxv. p. 342, 1924) in the furnace at a temperature of 1500° C.



*Discussion of the Results.*

The lines of iron have been classified by Walters, Catalán, Goudsmit, and put in a final form by Laporte \*. The constitution of the spectrum is in many respects similar to that of chromium, which was first classified by Catalán †. Both consist of triplets, quintets, and septets with inter-combinations among the different systems. In both spectra many chief terms belong to the quintet system. For convenience of reference they are diagrammatically represented in Charts 1 and 2.

## CHART 1.

## Spectrum of Iron.

*The Quintet System.*

					Term value.	Laporte's notation.
$n_{12}^5$					$x-39713.....\bar{s}$	
$n_{21}^5 \quad n_{22}^5 \quad n_{23}^5$					$x-29056.....p^1$	
-263.7 -413.0					$x-36766.....p^2$	
-252.0 -390.6					$x-42532.....p^3$	
-219.2 -327.0					$x-16372.....p$	
-200.0 -177.0						
$n_{30}^5 \quad n_{31}^5 \quad n_{32}^5 \quad n_{33}^5 \quad n_{34}^5$					$x-68000 (?)..d^1$	
-89.9 -184.1 -288.1 -415.9					$x-25900.....\bar{d}^1$	
-71.1 -139.7 -199.5 -240.2					$x-33095.....\bar{d}^2$	
-104.5 -215.5 -294.4 -411.2					$x-39625.....\bar{d}^3$	
-86.7 -173.2 -261.5 -344.0					$x-44677.....d^2$	
-86.0 -175.3 -273.6 -384.3						
$n_{41}^5 \quad n_{42}^5 \quad n_{43}^5 \quad n_{44}^5 \quad n_{45}^5$					$x-6928 .....f^1$	
-168.9 -257.7 -351.3 -448.5					$x-26874.....f^1$	
-106.8 -164.9 -227.9 -292.3					$x-33695.....f^2$	
-144.9 -218.4 -289.2 -344.1					$x-40257.....f^3$	
-112.3 -176.0 -247.7 -337.1						
$n_{51}^5 \quad n_{52}^5 \quad n_{53}^5 \quad n_{54}^5 \quad n_{55}^5$					$x-34782.....\bar{g}^1$	
					$x-42912.....\bar{g}^2$	

\* Laporte, *Zeits. für Physik*, vol. xxiii. p. 135, and vol. xxvi. p. 1. All the other references will be found there.

† Vide Gieseler, *Zeits. für Physik*, vol. xxii. p. 228 (1924).

## Constitution of the Spectrum of Iron.

The spectrum of iron as investigated by Laporte has been shown to consist of septets, quintets, and triplets, and each system consisting of parallel sets of "undashed" and "dashed" terms. The notation is that of Landé\*.

The highest terms so far obtained are five-fold  $d$ -terms of the quintet system. As the term values are not known with certainty, the largest term,  $d_4^1$ , is denoted by  $x$ . The other  $d^1$ 's are obtained by adding (in the algebraic sense) the corresponding frequency difference to  $d_4^1$ . Thus

$$d_3^1(n_{33}^5) = x - 415 \cdot 9, \quad d_2^1(n_{32}^5) = d_3^1 - 288 \cdot 1.$$

The negative value of the frequency difference shows that the terms are "Verkehrte" or "inverse."

The next highest term is  $\bar{f}_5^1$ , which is equivalent to  $x - 6928$ .

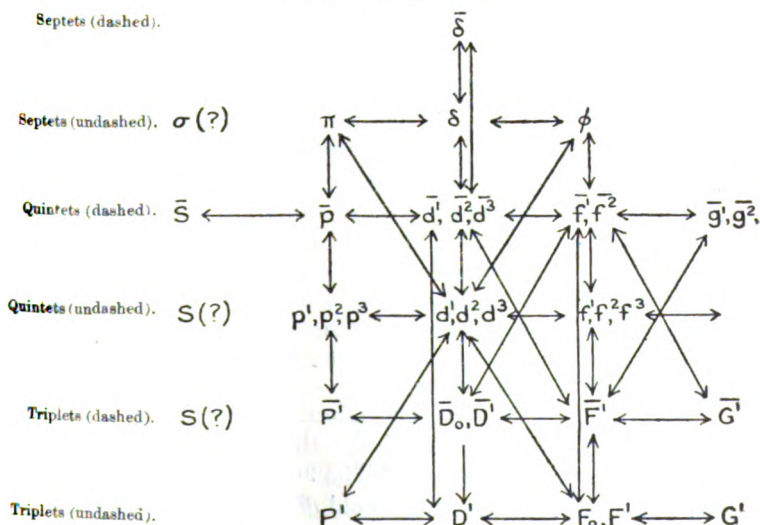
The next set is  $\bar{F}^1$  of the triplet system,  $\bar{F}_3^1 = x - 11976$ .

Lines having  $\bar{d}^1$ 's and  $\bar{f}^1$ 's as initial terms have come in absorption on certain plates only.

The combinations are represented in the following modified Laporte diagram (called henceforth "Key to the Iron-Spectrum") :—

Fig. 3.

Key to Iron Spectrum.



\* *Zeitschrift für Physik*, vol. xv. p. 191 (1923).

A glance at the chart shows that a term, say  $d^1$ , combines with those indicated by arrows, viz. with  $\bar{d}^1$ ,  $\bar{d}^2$ ,  $\bar{d}^3$ ;  $p^1$ ,  $p^2$ ,  $p^3$ ;  $f^1$ ,  $f^2$ ,  $f^3$ ;  $D_0$ ,  $\bar{D}^1$ ;  $\pi$ ,  $\phi$ ,  $P^1$ ,  $F_0$ ,  $F^1$ ; and breaks the selection principle of combining with  $g^1$ ,  $G^1$ , which is not shown in the chart. Similar remarks apply to every term shown in the key-diagram.

### CHART 2.

#### Spectrum of Chromium.

##### The Quintet System.

					Term
					Catalán's* value. notation.
$n_{12}^5$					46948.48 ... $1s^a$
$n_{21}^5$	$n_{22}^5$	$n_{23}^5$			
	-5.75	-8.76			27754.69 ... $2p^a$
	163.7	239.9			24717.86 ... $2p^c$
	52.6	60.6	Rydberg sequence	{	13499.30 ... $3p^c$
	7.8	15.5			9164.98 ... $4p^c$
$n_{30}^5$	$n_{31}^5$	$n_{32}^5$	$n_{33}^5$	$n_{34}^5$	
60.00	116.50	167.69	212.72		46233.96 ... $d^a$
86.0	118.4	129.4	144.6		Dashed { 20824.9 .. $d^b$
64.5	119.7	166.3	207.0		system { 13516.2 ... $d^c$
$n_{41}^5$	$n_{42}^5$	$n_{43}^5$	$n_{44}^5$	$n_{45}^5$	
	71.4	106.6	141.0	174.0	23262.10 ... $f^a$
	64.9	114.7	138.7	168.8	13149.2 ... $f^b$

\* Catalán, *Ann. Soc. Espan. Fis. y. Chim.* vol. xxi. p. 84 (1923).

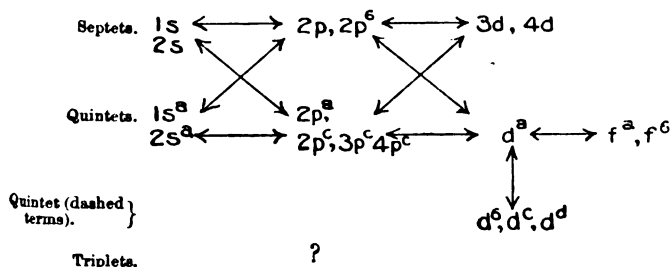
#### Constitution of the Spectrum of Chromium.

The spectrum of chromium consists of septets, quintets, and triplets. The highest term so far obtained is an  $1s$ -term of the septet system, *i. e.*  $n_{13}^7$ , having the value 54511.26. The septet lines  $1s-2p$ ,  $1s-2p^b$  constitute the strongest lines of the chromium spectrum, and were the only lines obtained by Gieseler and Grotrian in absorption in the furnace. They did not get even the  $1s^a-2p^a$  terms of the quintet system in absorption.

The quintet system of chromium has a  $1s$ -term, *i. e.*  $n_{12}^5$  having the value 46948.48. But this value is approached by 5-fold  $d^a$ -terms,  $n_{34}^5$  being 46233.96. According to our view, this corresponds to the 5-fold  $d^1$ -terms of iron, which are the highest terms obtained by Laporte ( $d_1^4$  in Laporte's notation).

The combinations of chromium are represented in the following Laporte diagram. The values are taken from Gieseler's \* paper.

Fig. 4.



### Comparison of the Spectra of Chromium and Iron.

A comparative study of the two charts shows that the greater complexity of the iron spectrum is entirely due to the full development of the "gestrichene" or the "dashed" system. These are only feebly developed in chromium ( $d^b, d^e, d^d$ ).

The question still remains open whether the quintet or septet system of iron may not contain a  $1s$ -term larger than the  $d^1$ 's.

### Analysis of Table I.

From analysis of Table I. we find that the following system of lines have been obtained in absorption :—

(a) Multiplets having  $d^1$ 's as initial orbits (*vide* key to iron spectrum).

- Multiplet 1.  $d^1 - p^1$ , all lines obtained excepting  $d_2^1 - p_3^1$ .
- " 2.  $d^1 - p^2$ , all lines.
- " 3.  $d^1 - \bar{d}^1$ , "
- " 4.  $d^1 - \bar{d}^2$ , "
- " 5.  $d^1 - \bar{d}^3$ , 9 lines out of 12 obtained.
- " 6.  $d^1 - f^1$ , all lines.
- " 7.  $d^1 - f^2$ , all lines except  $d_2^1 - f_1^2$ .
- " 24.  $d^1 - \bar{D}^1$ , very weak lines; 5 out of 9 obtained.

See under :

- Multiplet 24.  $d^1 - F^1$ , only 3 lines.
- " 23.  $d^1 - P^1$ , only 2 strongest out of 7 lines obtained.
- " 46 a.  $d^1 - \bar{g}^1$ , only 3 out of 9 obtained.
- " 46 b.  $d^1 - \bar{G}^1$ , only 2 lines obtained.

\* Gieseler, *Zeits. f. Phys.* vol. xxii. p. 228 (1924).

The last two are rather remarkable as the lines are weak and, as pointed out by Laporte, break the principle of selection.

(b) Multiplets having the next terms  $f^1$  as their initial orbits.

- Multiplet 10.  $\bar{f}^1 - \bar{d}^3$ , 8 out of 12 lines obtained.  
 „ 11.  $\bar{f}^1 - \bar{d}^3$ , 8 out of 12 lines obtained.  
 „ 13.  $\bar{f}^1 - f^2$ , 9 out of 13 lines obtained.  
 „ 14.  $\bar{f}^1 - f^2$ , only the strongest line obtained.  
 „ 15.  $\bar{f}^1 - \bar{g}^1$ , partially explored; only 2 lines obtained.  
 „ 26.  $\bar{f}^1 - \bar{G}^1$ , only 2 strongest out of 8 lines obtained.  
 „ 47.  $f^1 - \bar{g}^3 * ?$ , 9 out of 11 lines obtained.

\* Multiplet 47 was provisionally classified by Laporte to belong to  $f^1 - g^2$  combinations. The absorption experiment completely establishes the validity of the classification.

The line  $\bar{f}^1 - \bar{P}_2^1$  which breaks the principle of selection has also been obtained in absorption.

(c) On some plates, lines having the next highest terms  $\bar{F}^1$  of the triplet system have come out in absorption. This is reproduced in the plate.

- Multiplet 20.  $\bar{F}^1 - \bar{D}^1$ , all lines obtained except the two weakest.  
 „ 21.  $\bar{F}^1 - \bar{F}^1$ , the plate contains 3 lines out of 7.  
 „ 22.  $\bar{F}^1 - \bar{G}^1$ , no plate taken.

No other lines have come out in absorption.

According to Laporte's classification,  $d^1$ ,  $\bar{f}^1$ ,  $\bar{F}^1$  form the successive highest groups of terms. It is noteworthy that while on all plates lines having  $\bar{d}^1$ 's and  $f^1$ 's have come out in absorption, though the  $\bar{f}^1$ -combinations have come out rather faintly. The strong group of lines represented by the triplet combinations :

$$\begin{aligned} \bar{F}^1 - \bar{D}^1, \text{ strongest line, } \bar{F}_4^1 - \bar{D}_1^3, \lambda = 3815.84 (100r), \\ \bar{F}^1 - \bar{F}^1, \text{ strongest line, } \bar{F}_4^1 - \bar{F}_4^1, \lambda = 4045.82 (60r), \\ \bar{F}^1 - \bar{G}^1, \text{ strongest line, } \bar{F}_4^1 - \bar{G}_5^1, \lambda = 4271.76 (35), \end{aligned}$$

have come in absorption only on a few plates. On some plates they were obtained as emission lines.

None of the lines having the next highest terms  $\bar{d}^1$  have come out in absorption, while much less intense lines having  $d^1$ 's as their initial terms have been obtained in absorption.

We may refer to the group  $\bar{d}^1 - \bar{g}^1$ , which break the selection-principle, for here we have the azimuthal quantum number changing from 3 to 5.

$$\lambda = 2874.18 \text{ intensity } 10 \text{ (I), } d_4^1 - \bar{g}_5^1.$$

$$\lambda = 2869.31 \text{ intensity } 10 \text{ (I), } d_3^1 - \bar{g}_6^1.$$

One is reminded of Datta's work on the absorption spectrum of potassium vapour in which faint  $1s-md$  lines were obtained in absorption, but no  $2p-md$  or  $2p-ms$  lines, though in the emission spectrum the latter are much more intense. The analogy is quite complete.

The work thus confirms the validity of Laporte's classification of iron lines, but many absorption lines obtained still remain unclassified.

The potentiality of the method for studying the absorption spectra of elements seems to be very great, and if spectroscopes with greater resolving and light-gathering power are available, the water-spark can be made to give very good absorption spectra.

### Ionization Potential of Iron.

It may be mentioned in this connexion that on the basis of this and other absorption experiments, it is probably not safe to conclude that the  $d^1$ 's are the fundamental orbits of Fe.

For this purpose, the charts on the spectra of Fe and Cr may be compared. In chromium the highest term is  $1s$  of the septet system, and the next is  $1s^a$  of the quintet system. The  $d^a$ -terms of the quintet group of chromium give a very important set of lines in the chromium spectrum, and are thus analogous to the  $d^1$ -group of iron. But in the iron spectrum no term corresponding to the  $1s$ ,  $1s^a$  of chromium have been obtained. These are marked with a query mark in the key to the iron spectrum.

The question arises if, in the case of iron,  $1s$ -terms exist, and, if so, whether they have larger values than the  $d^1$ 's. Gerlach \* reports that some extraordinarily strong iron lines have been obtained in the water-spark between  $\lambda = 2000$  to  $\lambda = 2100$  A.U., and that these lines could not be fitted into Laporte's scheme. Unfortunately we have not been able to study this region with our apparatus. In the case of Cr, Gieseler and Grotrian † investigated the absorption spectrum

\* Gerlach, *Physik. Zeitschr.* vol. xxv. p. 620 (1924), and *Ann. der Physik*, vol. lxxvi. p. 197 (1925).

† Gieseler and Grotrian, *Zeits. f. Phys.* vol. xxii. p. 245 (1924).

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in the furnace at  $1250^{\circ}\text{C.}$ , but got only  $1s$ - $mp$  lines. No line beginning with  $1s^2$  or  $d^2$ 's were obtained in absorption. In the case of iron, on the other hand, the strong group  $d^1-\bar{d}^1$  was obtained in absorption at  $1250^{\circ}\text{C.}$ , so that this experiment may be interpreted as deciding against the existence of a higher  $1s$ -term. But we do not hold this sort of evidence to be decisive, because at the high temperature of the furnace it is quite possible that a large fraction of  $d^1$ -orbits are produced. Once they are produced they will remain fairly stable, for the transition  $d \rightarrow s$  being forbidden, the  $d$ -states will be metastable. This is supported by evidence from the chromospheric spectrum. The strongest lines in the iron spectrum,

$$\lambda = 3856.46 \text{ \AA.U. } d_3^1 - \bar{d}_2^1, \lambda = 3860.01 d_4^1 - \bar{d}_4^1,$$

reach in the solar chromosphere a height of 6000 km., and Evershed \* notes that they are intensified from intensity 8 (Rowland's scale) in the Fraunhofer spectrum to 15 in the flash spectrum. This behaviour is typical of lines arising from metastable orbits. If the higher  $1s$ -term exists at all, the value will be in the neighbourhood of 80,000, corresponding to an ionization potential about 10 volts. This point and other points mentioned in the paper are receiving attention.

*Summary.*

The paper describes an experimental work on the absorption spectrum of iron, which is obtained when the high-frequency spark produced between two iron electrodes immersed in distilled water is analysed by a spectroscope. The exact experimental conditions are described in detail, and the results obtained are compared with the recent work of Laporte on the classification of iron lines. It is shown that all multiplets having the three highest groups of terms, viz.  $d^1$ ,  $f^1$  and occasionally  $F^1$ , as initial orbits, are obtained in absorption. Some weak lines are also obtained in absorption which are shown to correspond to the transition of the azimuthal quantum number from  $k$  to  $k+2$  (violation of Sommerfeld's selection-principle). It is shown that this method of obtaining absorption spectra is as suitable as the more elaborate method of obtaining it in the furnace. Arguments are advanced in support of the view that iron may have a term higher than the  $d$ -term which is the highest so far obtained.

I take this opportunity of recording my sincere thanks to Prof. M. N. Saha for his guidance and interest in the work.

\* Evershed, *Phil. Trans.*, vol. cci. p. 474 (1901).

XXXVI. *On the Absorption Spectra of Aluminium and Cobalt.* By N. K. SUR, M.Sc., and K. MAJUMDAR, M.Sc.,  
Department of Physics, University of Allahabad\*.

*Introductory.*

IT is generally acknowledged that the study of the absorption spectra of elements provides us with the simplest method of determining the normal states of atoms, and thus affords a clue to the analysis of their spectra. The first systematic study was made by Wood† and Bevan‡, and afterwards corroborated in certain cases by McLennan§. They proved that in the case of elements of the first and second groups the normal orbits are those designated spectroscopically by 1s and 1S respectively.

The subject has acquired great importance in connexion with the classification of series spectra of the group of elements from Sc to Ni and of the elements of the third group. A few years ago it was believed from analogy that, in the case of every element, the lowest energy level corresponded to a 1S-term, having the azimuthal quantum number 1 and radial quantum number 0. But it was found from analysis of the spectra of metals of the third group that the largest series term was in every case a 2p-term||. This fact was also corroborated by the absorption experiments of Grotrian¶, Carroll\*\*, and Narayan††; in the case of thallium, indium, and gallium, they showed that the first lines to come out in absorption at the lowest temperatures were 2p<sub>2</sub>-ms and 2p<sub>1</sub>-ms.

Similar absorption experiments have been carried out in the case of the elements Sc, Ti, V, Cr, Mn, and Fe by Grotrian and Gieseler‡‡, and in certain cases by Angerer and Joos§§. They have obtained results which are quite subversive of the earlier notions (viz. in every case the highest term is 1S), but which generally support the results obtained

\* Communicated by Prof. M. N. Saha.

† Wood and Fortrat, *Astrophys. Journ.* vol. xliii. p. 73 (1916).

‡ Bevan, *Proc. Roy. Soc. Lond. A*, vol. lxxxiii. p. 421, vol. lxxxv. p. 54 (1910).

§ McLennan and Ireton, *Phil. Mag.* vol. xxxvi. p. 461 (1913); McLennan, *Proc. Phys. Soc. Lond.* vol. xxxi. p. 1 (1918).

|| Fowler, 'Report on Series Spectra,' chap. xvii.

¶ Grotrian, *ZS. f. Phys.* vol. xii. p. 218 (1922).

\*\* Carroll, *Proc. Roy. Soc. Lond. A*, vol. ciii. p. 334 (1923).

†† Narayan, *Proc. Roy. Soc. Lond. A*, vol. cvi. p. 596 (1924).

‡‡ Grotrian and Gieseler, *ZS. f. Phys.* vol. xxv. pp. 165, 342 (1924).

§§ Angerer and Joos, *Ann. d. Phys.* vol. lxxiv. p. 743 (1924).



from straightforward analysis of the spectra of these elements, carried out recently by Catalán, Kiess and Kiess, Meggers, Laporte, and others. These results are summarized below in Table I.

TABLE I.

Element.	Designation.	Landé's symbol.	Remarks.
19 K .....	1s	$n_{11}^2$	
20 Ca ...	1S	$n_{10}^1$	
21 Sc ...	D or P?	$n_{22}^2$ or $n_{33}^2$	Catalán and Grotrian, <i>Zeits. f. Phys.</i> xxv. p. 362 (1924).
22 Ti.....	f	$n_{44}^3$	Kiess and Kiess, <i>Journ. Opt. Soc. Am.</i> viii. p. 607 (1924).
23 Va ...	F	$n_{45}^4$	Bechert and Sommer, <i>Zeits. f. Phys.</i> xxxi. p. 158 (1925).
24 Cr ...	1s	$n_{13}^7$	Gieseler, <i>Zeits. f. Phys.</i> xxvi. p. 228 (1924).
25 Mn ...	1S	$n_{14}^8$	Catalán, <i>Phil. Trans. Roy. Soc. Lond.</i> cccxiii. p. 127 (1922).
26 Fe ...	d	$n_{34}^5$	Landé, <i>Zeits. f. Phys.</i> xv. p. 191 (1923).
27 Co ...		$n_4^4$	Laporte, <i>Zeits. f. Phys.</i> xxiii. p. 135 (1924).
			Catalán and Bechert, <i>Zeits. f. Phys.</i> xxxii. p. 336 (1925).

The above summary shows that it is almost hopeless to deduce any general conclusion regarding the quantum specification of the normal orbits. Only Cr and Mn behave in a normal way, *i. e.* the 1s-terms are the largest. But in other cases 2p-, d-, or even f-terms have been found to be the highest.

The investigations reported below were undertaken in order to make a systematic study of the whole range of phenomena from the following standpoints:—

- (1) To study the absorption spectra of elements which are still unknown, and thus obtain a clue to their constitution; and
- (2) To study the variation of the absorption spectra under different temperatures and pressures, and thus make a systematic study of the production of higher orbits.

Thus at the lowest temperature Na vapour absorbs only 1s–mp lines. The problem before us is to find out at what temperature it will begin to absorb 2p–ms, or md-lines, and in what proportion?

King \* has found that the 2p-orbits of Na are produced in sufficient quantity only at temperatures of 2000° C., while experiments carried out in this laboratory show that a temperature of 1250° C. is generally sufficient. Grotrian and Gieseler † have found that if there is a set of orbits very close to the lowest orbits, as is generally the case with the higher elements, the absorption spectra that arise generally consist of lines proceeding from both sets, and it is not possible to mark out a stage when only one class appears in absorption to the exclusion of the next. Thus, in the vanadium spectrum, the lowest level is the F'-term of the quartet system, the next level being given by  $\bar{d}'$  of the sextet system. But the difference between the two sets is only  $\Delta\nu = 2112.5$ . In the absorption spectra lines with F' and  $\bar{d}'$ , combinations come out simultaneously and almost with the same strength. Thus the absorption spectra lose much of their pristine simplicity, and become more complex than desirable.

We have, therefore, designed an apparatus in which the temperature, as well as the quantity of material, could be varied continuously. We have first studied the absorption spectra of aluminium, cobalt, and nickel. Aluminium was chosen because its absorption spectrum had not yet been obtained. Cobalt and nickel were chosen because they are the only elements in the third horizontal row of the periodic table of which the series classifications were still unknown. Results obtained with Al and Co are reported below.

### *Apparatus.*

The metal was vaporized within a vacuum furnace of the type designed first by King and used subsequently by Saha ‡, Grotrian, and others. A sketch of the furnace is given in fig. 1.

### *Description of the Furnace.*

The furnace consists of a thin tube F of Acheson graphite, which was heated by a current taken from a set of heavy-discharge accumulators. We used 5 cells, and the voltage across the terminals was found to be 8.5 volts instead of 10. The loss is due to the resistance in the connecting leads, which consisted of thick copper wires enclosed within hose-pipes through which water was kept circulating. The current was taken through two parallel pools of mercury, and contact was made by a thick sliding copper piece. This served the

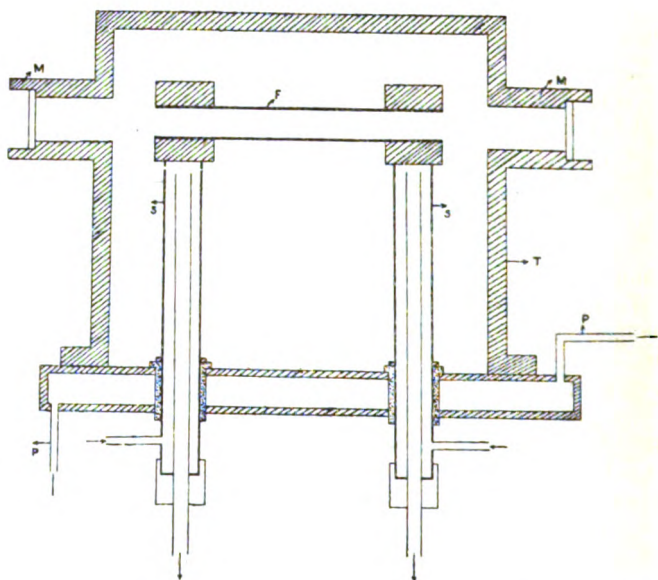
\* King, *Astrophys. Journ.* vol. lv. p. 354 (1922).

† Grotrian and Gieseler, *ZS. f. Phys.* vol. xxv. p. 342 (1924).

‡ Saha and Sur, *Journ. Ind. Chem. Soc.* vol. i. p. 9 (1924).

double purpose of a switch as well as an adjustable resistance. By sliding the contact piece along the pools of mercury, the terminal voltage could be reduced to any value. The highest temperature obtained was  $2100^{\circ}\text{C}$ . The current, on measurement, was found to be 680 amperes.

Fig. 1.



The construction of the furnace is apparent from the diagram. There was a side tube (not shown) which was closed by means of a quartz plate. Temperature could be measured by means of a Wanner pyrometer placed on this side. This was calibrated by Mr. Kampta Prasad by taking the melting-points of  $\text{NaCl}$  and  $\text{Cu}$  as standards. The furnace was shielded by a concentric iron mantle with a hole facing the quartz window.

#### *Spectroscopic Arrangement.*

Continuous light from a copper water-spark was rendered parallel by means of a quartz lens and allowed to traverse the furnace. The beam was then focussed on the slit of a concave grating which has a radius of 5 feet and a ruled surface of 1.5 inches. The mounting is of the Rowland type, giving a dispersion of  $11.11 \text{ \AA.U. per mm.}$  in the first order. Some photographs were taken in the second order as well.

The source of continuous light was a high-frequency oscillatory spark between copper electrodes immersed in

distilled water. The principal lines of copper  $\lambda=3273\cdot95$ ,  $\lambda=3247\cdot55$  always came on the continuous background as absorption lines, and served as fiducial points. The source was so brilliant that an exposure of 1-2 minutes was quite sufficient for the first-order spectrum.

*Aluminium.*

As has been already mentioned, Grotrian has corroborated by absorption experiments that in the case of indium, gallium, and thallium the  $2p$ -orbit is the normal state. His absorption experiments with Al were not fruitful, as he used silica tubes closed by quartz plates, which are strongly attacked by Al at high temperatures. Moreover, Al yields very little vapour up to  $1200^\circ\text{C}$ . By using the graphite furnace and heating it up to  $1520^\circ\text{C}$ ., the pair

$$\lambda=3961\cdot54 \text{ and } \lambda=3944\cdot03 (2p-2s)$$

came out reversed. At  $1650^\circ\text{C}$ . the leading members of  $2p-md$  series were obtained in reversal, and at  $1725^\circ\text{C}$ . the second pair of  $2p-ms$  series was also obtained in absorption. It may be mentioned that on all plates the lines at  $\lambda=2874\cdot24$  and  $\lambda=2450\cdot10$  belonging to the  $2p-md$  series of gallium, and the line at  $\lambda=4172\cdot06$  of the  $2p-ms$  series were also obtained in absorption.

TABLE II.

Aluminium lines obtained as reversals.

Sharp Series.	
( $\lambda$ .)	Series notation.
3961·54	$2p_1-2s$
3944·03	$2p_2-2s$
2660·39	$2p_1-3s$
2652·48	$2p_2-3s$
Diffuse Series.	
3092·84 }	$2p_1-3d_1$ ( $i=1$ or $2$ not resolved)
92·72 }	
3082·16	$2p_2-3d_2$
2575·41 }	$2p_1-4d_1$
75·11 }	
2567·99	$2p_2-4d_2$
2373·36 }	$2p_1-5d_1$
73·13 }	
2367·06	$2p_2-5d_2$
2269·21 }	$2p_1-6d_1$
69·03 }	
2263·45	$2p_2-6d_2$
2210·05	$2p_1-7d_1$ (on one plate only)

As the photographs were taken in the first-order spectrum of the concave grating, the dispersion was not sufficient to separate the  $2p_1-md_1$  and  $2p_1-md_2$  lines of the diffuse series.

A line at  $\lambda = 3057.16$  was also obtained on one plate, but we could not trace it to its source.

From this experiment it results that the lines which appear in absorption belong to the subordinate series of aluminium, for which the  $2p$ -terms represent the initial states.

It must be mentioned here, however, that it is not possible to deduce from such experiments whether, for aluminium, the  $2p$ -terms represent the normal orbits or not. For, at the temperature at which sufficient vapour is available for absorption experiments, the thermal stimulus is high enough to convert an appreciable fraction of possible  $1s$ -orbits to the  $2p$ -stage. A positive answer can be given by simultaneous measurement of the vapour-pressure of aluminium, which is still unknown, and from measurement of the dispersion of Al vapour, which will give the number of centres of absorption, *i. e.* atoms in  $2p$ -orbits. If the ratio of the number of absorption centres to the number of atoms present be of the order unity, then and then only we can maintain that  $2p$  is the normal state of Al-atoms. Such experiments have been done by Ladenburg and Loria \* in the case of hydrogen (excited by electric spark), who found that 1 in 50,000 of the atoms are excited to the  $2p$  orbit, and by Hallo † and Geiger ‡ in the case of Na. who found that 1 atom in 12 can act as absorption centres for  $D_1$  and  $D_2$ . This shows that  $D_1$  and  $D_2$  arise from normal orbits, while  $H\alpha$  of hydrogen arises from a higher orbit.

NOTE.—It may be worth recording in this connexion that in attempting to study spectroscopically the thermal ionization of calcium vapour, a rather interesting fact was observed. At about  $800^\circ \text{C.}$ , the  $g$ -line of Ca is not obtained in absorption, though the vapour-pressure is quite sufficient. A band spectrum was obtained extending roughly from  $3150 \text{ \AA.U.}$  to  $4100 \text{ \AA.U.}$  At low temperatures, Ca and probably the other alkaline earths are in a diatomic state. This is also confirmed by the vapour-pressure experiments of Ruff and Hartmann (*vide Zeits. für Anorg. und Allg. Chemie*, cxxxiii. pp. 29–45, 1924). They have found from vapour-pressure data that the chemical constant has a value which is abnormally high, if we suppose Ca to be monatomic. According to Nernst's theory,  $C = -1.62 + \frac{3}{2} \log M$ . Taking  $M = 40$ , the chemical constant of monatomic calcium ought to be 0.78, while Ruff and Hartmann find it to be 3.44. This indicates that at a temperature of  $800^\circ \text{C.}$ , calcium is diatomic, while at higher temperatures it is broken up into atoms.

\* Ladenburg and Loria, *Verh. d. D. Phys. Ges.* vol. x. p. 858 (1908).

† Hallo, *Phys. Zeits.* vol. iv. p. 545 (1903).

‡ Geiger, *Ann. d. Phys.* vol. xxiv. p. 597 (1907).

## Cobalt.

Angerer and Joos have performed absorption experiments with cobalt in a different type of furnace. The lines obtained by them are marked "A" under the heading "Remarks" in Table III., in which the wave-length of lines of cobalt

TABLE III.

Absorption lines of Cobalt in the furnace.

Wave-length I.A. (Dhein).	Wave-number (vacuum).	Intensity and class (King).	Series classification (Catalán & Bechert *).	Multiplet number (Catalán & Bechert).	Remarks.
4190.709	23855.61	20 I	$f_5^1 - \phi_5^1$	71	
76.134	24526.15	3 Ia	$f_3^2 - f_3^1$	28	
4027.044	24825.12	10 I	$f_3^1 - r_4^1$	73	
3997.909	25006.03	40 II	$F_3^1 - f_4^2$	64	
3995.312	25022.08	60 II	$F_4^1 - g_5^2$	67	
3961.006	25238.99	6 II	.....	...	not classified
3945.323	25339.32	15 I	$F_4^1 - F_3^1$	6	
3909.941	25568.62	15 I	$f_5^1 - r_6^1$	73	
3894.981	25666.82	20 II	$f_2^2 - d_1^1$	22	just separated
3894.086	25672.72	6 II	$F_3^1 - G_4^2$	9	
3873.957	25806.10	40 II	$f_4^2 - d_3^1$	22	just separated
3873.117	25811.70	60 II	$f_5^2 - d_5^1$	22	
3845.474	25997.24	60 II	$F_4^1 - G_5^2$	9	
3745.501	26691.14	25 I	$F_4^1 - G_4^2$	9	
3631.340	27530.23	20r II	$f_4^1 - f_5^1$	25	
3627.807	27557.03	25r I	$f_4^2 - G_5^1$	58	
3624.955	27578.71	8 I	$f_2^2 - d_3^1$	23	
3604.469	27735.45	4 II	.....	...	not classified
3602.081	27753.84	40R II	$f_2^1 - \bar{f}_2^1$	25	
3594.869	27809.52	50R II	$f_3^1 - \bar{f}_3^1$	25	
3585.159	27884.84	20R I	$f_4^2 - d_4^2$	23	not resolved
3584.796	27887.66	15 I	$f_3^1 - d_4^1$	19	
3575.361	27961.25	60r II	$f_4^1 - \bar{f}_4^1$	25	not resolved
3574.964	27964.36	25r I	$f_3^2 - d_3^2$	23	
3569.382	28008.10	80R II	$F_4^1 - \bar{F}_4^2$	7	
3564.955	28042.87	25r I	$f_3^2 - G_4^1$	58	
3560.896	28074.83	20r I	$f_2^2 - d_2^2$	23	
3533.363	28296.60	25r I	$f_2^1 - g_3^1$	31	

\* Catalán and Bechert, *Zs. f. phys.* vol. xxxii. pp. 336-369 (1925).



TABLE III. (continued.)

Wave-length I.A. (Dhein).	Wave- number (vacuum).	Intensity and class (King).	Series classification (Catalán & Bechert).	Multiplet number (Catalán & Bechert).	Remarks.
3529.815	28322.03	80R II	$f_4^2 - g_5^2$	35 } ...	A just resolved
3529.037	28325.06	30R I	$f_3^1 - g_4^1$	31 }	
3526.856	28345.79	100R II	$f_5^1 - f_5^1$	25.....	A
3523.438	28373.28	25r I	$f_2^2 - d_1^2$	23	
3521.572	28388.32	30r I	$f_5^2 - f_4^1$	54	
3520.087	28400.29	15 I	$f_4^1 - f_3^1$	25	
3518.353	28414.29	50R II	$F_3^1 - D_2^2$	5	
3513.483	28453.68	50R II	$f_4^1 - g_5^1$	31	
3512.643	28460.49	60R II	$f_3^2 - d_2^2$	23	
3510.419	28478.52	30r I	$f_4^1 - d_4^1$	19 } ...	A not resolved
3509.844	28483.19	50r II	$f_3^2 - g_4^2$	35 }	
3506.315	28511.85	80R II	$f_2^2 - d_3^2$	23	
3502.281	28544.69	100R II	$f_5^2 - d_4^2$	23.....	A
3495.685	28598.53	50r II	$f_2^2 - g_3^2$	35	
3491.324	28634.27	15 I	$f_2^1 - d_2^1$	19 {	not resolved
3490.741	28639.04	10 I	$f_4^2 - F_3^1$	54 }	
3489.406	28650.00	60r II	$F_4^1 - D_3^2$	5	
3483.415	28699.28	20r I	$f_4^2 - f_5^2$	29	
3474.019	28776.90	100R II	$f_3^2 - f_4^2$	29.....	A
			$f_5^1 - f_4^1$	25.....	A
3465.796	28845.18	100R II	$f_5^1 - g_6^1$	31.....	A
346.807	28870.07	60r II	$f_2^2 - f_3^2$	29	
3453.513	28947.75	200R II	$f_5^2 - g_6^2$	35.....	A
3449.443	28981.91	60R II	$f_5^2 - g_5^2$	35 {	not resolved
3449.171	28984.20	60R II	$f_3^2 - g_3^2$	35 }	
3443.646	29030.70	80R II	$f_4^2 - g_4^2$	35.....	A
3433.043	29120.36	60R II	$f_2^2 - f_2^2$	29	
3412.636	29294.48	80R II	$f_5^1 - d_4^1$	19 } ...	A not resolved
3412.335	29297.07	80R II	$f_4^2 - G_5^2$	59 } ...	
3409.176	29324.21	60r II	$f_4^2 - f_4^2$	29	
3405.120	29359.15	150R II	$f_5^2 - f_5^2$	29.....	A
3395.378	29443.38	40r II	$f_3^2 - G_4^2$	59	
3385.227	29531.67	25r II	$f_4^2 - g_3^2$	35	
3367.114	29690.52	30r II	$f_5^2 - g_4^2$	35	
3354.386	29803.17	20R II	$f_4^2 - f_3^2$	29	
3334.151	29984.05	30r	$f_5^2 - f_4^2$	29	

TABLE III. (continued).

Wave-length I.A. (Dhein).	Wave-number (vacuum).	Intensity and class (King).	Series classification (Catalán & Bechert).	Multiplet number (Catalán & Bechert).	Remarks.
3249.994	30760.44	6 II	$f_3^2 - \bar{F}_4^2$	55	not classified
3247.176	30787.13	8 II	.....	...	
3159.660	31639.84	10 II	$f_3^2 - \bar{F}_3^2$	55, 20	not clearly separated
3158.769	31648.78	12 II	$f_2^1 - d_1^2$		
3147.060	31766.51	15r II	$f_4^1 - g_5^2$	32	not resolved
3137.325	31865.08	10 II	$f_3^1 - g_4^2$	32	
3121.560	32026.01	12R II	$f_2^1 - g_3^2$	32	
3121.414	32027.51	12R II	$f_4^1 - f_5^2$	26	
3072.346	32538.99	15r II	$f_5^1 - d_4^2$	20	
3064.375	32623.62	5 II	$f_3^1 - f_3^2$	26	
3061.825	32650.80	20r II	$f_4^1 - G_5^2$	57	A
3048.892	32789.29	12r II	$f_4^1 - \bar{f}_4^2$	26	
3044.007	32841.91	30R II	$f_3^1 - \bar{f}_3^2$	26	
3034.426	32945.59	6 II	$f_5^1 - \bar{f}_5^2$	26.....	
2987.172	33466.74	15r II	$f_3^1 - \bar{D}_2$	48	
			$f_5^1 - \bar{f}_4^2$	26	
Wave-length I.A. (Dhein).	Wave-number (vacuum).	Intensity (Dhein).	Series classification (Catalán & Bechert).	Multiplet number (Catalán & Bechert).	Remarks.
2842.388	35171.37	3	.....	...	not classified
2833.928	35276.36	1	$f_4^1 - D_3^2$	49	not classified
2814.979	35213.81	2	$f_4^1 - \bar{F}_3^2$	53	
2663.531	37533.00	4	.....	...	
2650.271	37720.77	4	$f_2^2 - \bar{f}_2^3$	30	
Wave-length I.A. (Krebs).	Wave-number (vacuum).	Intensity (Krebs).	Series classification (Catalán & Bechert).	Multiplet number (Catalán & Bechert).	Remarks.
2574.366	38832.90	3R	$f_4^1 - d_4^3$	21	A
2544.330	39291.28	2	$f_2^1 - d_1^3$	21.....	
2528.968	39529.95	3R	$f_4^1 - d_3^3$	21.....	A
2424.938	41225.63	3R	$f_5^1 - f_5^3$	27	A
2407.260	41528.35	3R	$f_5^1 - g_6^3$	33.....	
2354.825	42452.94	2	.....	.....	A not classified



obtained by us in reversal are noted. It will be seen that we have obtained more lines than Angerer and Joos\*. On the short wave-length side the work is not yet complete. The graphite tube was heated to  $1950^{\circ}$  C. or  $2000^{\circ}$  C. Apparently, cobalt does not give sufficient vapour at lower temperatures. The wave-lengths are taken from the measurements of Dhein†.

### Analysis of Table III.

After this work was completed, Catalán and Bechert published a paper‡ in which the series classification of cobalt lines has been worked out. From a comparison of our data with Catalán's work, we find that lines belonging to the following multiplets have been obtained in absorption. We also append a key of the cobalt spectrum for explaining the combinations:—

(a) Lines belonging to multiplets having  $f^1$  as initial orbits:—

Multiplet 19,  $f^1d^1$ —four lines obtained.

„	20, $f^1d^2$ —two	„	„
„	21, $f^1d^3$ —three	„	„
„	25, $f^1f^1$ —seven	„	„
„	26, $f^1f^2$ —six	„	„
„	27, $f^1f^3$ —one line	„	„
„	31, $f^1g^1$ —four lines	„	„
„	32, $f^1g^2$ —three	„	„
„	33, $f^1g^3$ —one line	„	„
„	48, $f^1D^1$ —	„	„
„	49, $f^1D^2$ —	„	„
„	53, $f^1F^2$ —	„	„
„	57, $f^1G^2$ —	„	„
„	71, $f^1\phi^1$ —	„	„
„	73, $f^1\gamma^1$ —two lines	„	„

(b) Lines belonging to multiplets having  $f^2$  as initial orbits:—

Multiplet 22,  $f^2d^1$ —three lines obtained.

„	23, $f^2d^2$ —eight	„	„
„	28, $f^2f^1$ —one line	„	„
„	29, $f^2f^2$ —eight lines	„	„
„	30, $f^2f^3$ —one line	„	„
„	35, $f^2g^2$ —nine lines	„	„
„	54, $f^2F^1$ —two	„	„
„	55, $f^2F^2$ —	„	„
„	58, $f^2G^1$ —	„	„
„	59, $f^2G^1$ —	„	„

\* Angerer and Joos, *Ann. d. Phys.* vol. lxxiv. p. 755 (1924).

† Dhein, Kayser-Konen's *Handbuch der Spectroskopie*, vol. vii.

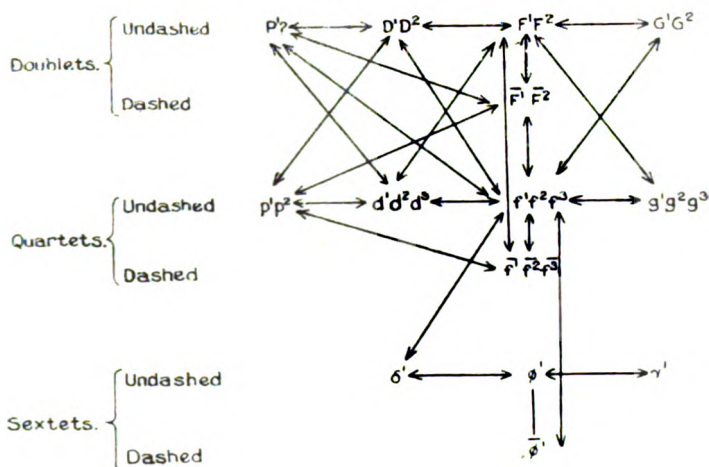
‡ *Zs. f. Phys.* vol. xxxi. p. 336 (1925).

(c) Lines belonging to multiplets having  $f^1$  as initial orbits:—

Multiplets 5,  $F^1D^2$ —two lines obtained.

„ 6,  $F^1F^1$ —one line „  
 „ 7,  $F^1F^2$ — „ „ „  
 „ 9,  $F^1G^2$ —three lines „  
 „ 64,  $F^1f^2$ —one line „  
 „ 67,  $F^1g^2$ — „ „ „

Fig. 2.



Key to Cobalt Spectrum.

The different combinations as shown by the arrows in the above diagram have been obtained by Catalán and Bechert. According to them the term  $P^1$  is uncertain.  $f^1, f^2, F^1$  are the biggest terms.

### Discussion of Results.

According to the classification of the arc-spectrum of cobalt by Catalán and Bechert,  $f^1, f^2$ , and  $F^1$  form the three closely successive highest groups of terms. Lines belonging to the  $f^1$  and  $f^2$  groups have come out prominently in absorption, while a few strong lines belonging to the  $F^1$  group have also been obtained. The absorption experiment definitely points to the fact that an  $f$ -term is the fundamental term of the cobalt arc-spectrum; but it is to be noted here that this is not in agreement with Bohr and Stoner's scheme of the periodic system, according to which a  $d$ -term is to be expected as the fundamental term. It is not possible to decide

from this experiment whether  $f^1$  or  $f^2$  is the fundamental term ;  $f^1$  or  $f^2$  corresponds to two close levels, the difference in these term-values being about  $3500^{-1}$  cm., and, at the temperature necessary for the absorption experiment, transitions to the orbits corresponding to  $f^1$  and  $f^2$  terms are equally probable, as is shown by the lines absorbed. A clue to this would probably be obtained by pushing the experiment further in the ultra-violet region.

The lines belonging to the group  $f^1\bar{\phi}^1$  are intercombination lines, and Catalán and Bechert have suggested them to be the resonance lines ; but only one line,  $\lambda=4190\cdot709$  (I.A.), of this group was obtained in absorption. This is the strongest line of the suggested system of resonance lines, and the other weaker lines lie on the longer wave-length side of this line. Photographs were taken in this region, but no other line could be obtained in absorption. It appears that the group of lines  $f^1\bar{\phi}^1$  is not important enough to be regarded as the resonance lines.

### *Summary.*

The paper contains an account of experimental work on the absorption spectra of aluminium and cobalt in the high-temperature furnace. The  $2p_1-2s$ ,  $2p_2-2s$  lines of Al do not come in absorption before a temperature of  $1520^\circ$  C. is reached. The higher members of  $ps$ - and  $pd$ -series are obtained in absorption at about  $1700^\circ$  C.

The absorption spectrum of cobalt has been photographed from 4500 Å.U. to 3000 Å.U. at a temperature of  $2000^\circ$  C. The lines have been identified by measurement, and tabulated according to the series classification of Catalán and Bechert. It is shown that many lines belonging to  $f^1$  and  $f^2$ , and a few lines belonging to  $F^1$  terms, which are the three successive largest terms, have been obtained in absorption. Only one line,  $\lambda=4190\cdot709$ , belonging to the group which Catalán and Bechert have suggested for the resonance lines has come out in absorption.

We take this opportunity to express our sincere thanks to Prof. M. N. Saha for his guidance and interest in the work.

XXXVII. *The Determination of Young's Modulus from Compression Tests on Circular Cylinders.* By F. E. RELTON, B.A., B.Sc., Building Research Station, Department of Scientific and Industrial Research\*.

THE present paper owes its genesis to the call for an explanation of certain anomalies in the behaviour of specimens under compressive loads. These anomalies, which were rendered visible by the use of translucent specimens, were more apparent than real, being nothing more than the fact that plane horizontal sections did not remain plane under load; but they served to show that the compression test, as usually carried out, did not necessarily give the true value of Young's Modulus, despite the refinements of physical measurement of which modern extensometers are capable. It has been claimed for these instruments that they are capable of measuring down to  $10^{-6}$ , and even  $10^{-6}$ , of an inch. It became a matter of interest, and of some practical importance, to inquire to what extent the method was in itself reliable as a means of determining the particular physical constant. If the claims put forth on behalf of the extensometers were valid, one could measure a movement to within 0.2 per cent. of its true value; but such refinement is futile unless the method can be made at least as reliable as this.

Of the literature on the subject I have made most use of a paper by Prof. L. N. G. Filon†; of papers subsequent thereto I have consulted one by Dr. J. Dougall‡. The former of these contains a section devoted to historical references, and no further mention thereof will here be made. In those portions of Filon's paper which are relevant to the present discussion, the analysis is limited by the assumption that no movement takes place at the periphery of the end face of the test piece; afterwards a correction is made for the case where there is movement of known amount. In actual practice it would be exceedingly difficult to say precisely what the magnitude of such movement would be; I have therefore so analysed the problem that no such measurement is necessary.

\* Communicated by the Director.

† "On the Elastic Equilibrium of Circular Cylinders under Certain Practical Systems of Load," Phil. Trans. Roy. Soc. ser. A, vol. cxviii. (1902).

‡ "An Analytical Theory of the Equilibrium of an Isotropic Elastic Rod of Circular Section," Trans. Roy. Soc. Edinb. vol. xlix. (1913-14).

The present paper falls into three sections, of which two are quite short. The first section seeks to explain why plane sections do not necessarily remain plane after loading. The second section determines the conditions requisite for a correct evaluation of Young's Modulus and Poisson's Ratio. The third section seeks to give a method of determining Young's Modulus even when the conditions laid down in the second section are violated. Though the applications of the paper are Mechanical rather than Mathematical, the treatment can hardly be described as elementary, and as the third section is somewhat long an indication of its mode of development will be given here.

It can be shown that when the displacements in a body are symmetrical about an axis, the strains and principal stresses can all be expressed in terms of a single function which satisfies a partial differential equation of the fourth order. The number of solutions to this equation is infinite, but two types are chosen :—

- (i.) solutions involving circular and Bessel functions,
- (ii.) a finite polynomial.

From these a solution is formed by multiplying them by constants and combining them additively. This solution is then made to fit the requisite boundary conditions, thereby establishing certain relations among the constants. By a suitable choice it eventuates that the number of these relations is adequate to the solution of the problem. No cognisance is taken of the actual distribution of the load provided it be symmetrically disposed about the axis. The contraction of a known length and the extension of a diameter of the mid-section are computed ; these can be measured by extensometers, and on these measurements the calculation of Young's Modulus is based. It appears in the sequel that the accurate determination of Young's Modulus is indissolubly bound up with a knowledge of the value of Poisson's Ratio.

## SECTION I.

In applying the Mathematical theory of Elasticity to the study of the behaviour of short cylinders in compression, there are certain obvious advantages in employing the cylindrical polar system of coordinates  $r, \theta, z$  ; where  $z$  is measured along the axis of the cylinder,  $r$  is measured from this axis, and  $\theta$  from some axial plane of reference.

During a test, the load will, as far as possible, be applied symmetrically about the axis, and the resulting displacements may be regarded as symmetrical. This gives rise to certain simplifications of the fundamental equations: two of the three "rotations" of the polar element are obviously zero, viz., those about the axis of  $z$  and about the horizontal (radial) axis, while differentiations with respect to  $\theta$  disappear. The equilibrium equations are reduced from three to two in number.

If  $u, v, w$  denote displacements in the directions  $r, \theta, z$  respectively we have  $v=0$ , and for the strains (in the usual notation)

$$\left. \begin{aligned} e_{rr} &= \frac{\partial u}{\partial r}, & e_{zz} &= \frac{\partial w}{\partial z}, & e_{\theta z} &= e_{z\theta} = 0, \\ e_{\theta\theta} &= \frac{u}{r}, & e_{rz} &= \frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}. \end{aligned} \right\} \dots (1)$$

The dilatation

$$\Delta = \frac{\partial u}{\partial r} + \frac{u}{r} + \frac{\partial w}{\partial z}, \dots (2)$$

and for the "rotations" we have

$$\omega_r = \omega_z = 0, \quad 2\omega_\theta = \frac{\partial u}{\partial z} - \frac{\partial w}{\partial r}. \dots (3)$$

Certain experiments have been carried out on prisms of gelatinous material with coloured threads inserted. It was found that the threads, being originally horizontal, became curved as the prism was compressed. The explanation is as follows:—Working in cylindrical polar coordinates, without necessarily confining ourselves to symmetrical displacements, the assumption that horizontal plane sections remain plane and horizontal after loading is expressed analytically by the equations

$$\frac{\partial w}{\partial r} = 0 = \omega_\theta.$$

From equation (3), which gives the form of  $\omega_\theta$ , we have immediately  $\frac{\partial u}{\partial z} = 0$ , which shows that the radial displacement is independent of  $z$  and must be the same at all levels, including the end faces. The curving of the threads indicates that the free motion of the end faces was impeded.

## SECTION II.

For the stresses we have

$$\left. \begin{aligned} \widehat{rr} &= \lambda\Delta + 2\mu \frac{\partial u}{\partial r}, & \widehat{\theta z} &= \widehat{\theta r} = 0, \\ \widehat{\theta\theta} &= \lambda\Delta + 2\mu \frac{u}{r}, & \widehat{rz} &= \mu \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial r} \right), \\ \widehat{zz} &= \lambda\Delta + 2\mu \frac{\partial w}{\partial z}. \end{aligned} \right\} \quad (4)$$

Since we are concerned only with equilibrium conditions, and as there are no body forces in operation, the equilibrium equations are :

$$\left. \begin{aligned} \frac{\partial}{\partial r}(\widehat{rr}) + \frac{\partial}{\partial z}(\widehat{rz}) + \frac{\widehat{rr} - \widehat{\theta\theta}}{r} &= 0, \\ \frac{\partial}{\partial r}(\widehat{rz}) + \frac{\partial}{\partial z}(\widehat{zz}) + \frac{\widehat{rz}}{r} &= 0, \end{aligned} \right\} \quad \dots \quad (5)$$

which can be written as

$$\left. \begin{aligned} (\lambda + 2\mu) \frac{\partial \Delta}{\partial r} + 2\mu \frac{\partial \varpi_\theta}{\partial z} &= 0, \\ (\lambda + 2\mu) \frac{\partial \Delta}{\partial z} - 2\frac{\mu}{r} \frac{\partial}{\partial r}(r\varpi_\theta) &= 0. \end{aligned} \right\} \quad \dots \quad (6)$$

Suppose that the deformations are linear, i.e.  $u, w$  are linear functions of  $r, z$ ; so that we write

$$u = \alpha z + \beta r, \quad w = \alpha' z + \beta' r,$$

$$\text{whence} \quad \Delta = \alpha' + 2\beta + \alpha z/r.$$

Then

$$2\varpi_\theta = \frac{\partial u}{\partial z} - \frac{\partial w}{\partial r} = \alpha - \beta', \quad \text{and} \quad \frac{\partial \varpi}{\partial z} = 0.$$

The former of equations (6) then shows that  $\frac{\partial \Delta}{\partial r} = 0$ , i.e.  $\Delta$  is independent of  $r$ , whence  $\alpha = 0$ , leaving  $\Delta = 2\beta + \alpha'$ , whence  $\frac{\partial \Delta}{\partial z} = 0$  and  $2\varpi_\theta = -\beta'$ . The latter of equations (6) now shows that  $\frac{\partial}{\partial r}(r\varpi_\theta) = 0$ , so that  $\beta' = 0$ . Consequently

$$u = \beta r, \quad w = \alpha' z, \quad \Delta = 2\beta + \alpha'.$$

From equations (4) we have

$$\begin{aligned}\widehat{rr} &= \lambda\Delta + 2\mu \frac{\partial u}{\partial r} \\ &= \lambda(2\beta + \alpha') + 2\mu\beta \\ &= \lambda\alpha' + 2\beta(\lambda + \mu).\end{aligned}$$

If no force is applied to the curved surface,  $\widehat{rr}=0$  at the boundary and we deduce

$$\frac{\lambda}{2(\lambda + \mu)} = -\frac{\beta}{\alpha'}.$$

Similarly

$$\begin{aligned}\widehat{zz} &= \lambda\Delta + 2\mu \frac{\partial w}{\partial z} \\ &= \lambda(2\beta + \alpha') + 2\mu\alpha' \\ &= \alpha'(\lambda + 2\mu) + 2\beta\lambda = -P, \text{ say,}\end{aligned}$$

which means that the end pressure is uniform and normal to the face inwards. We deduce

$$\left. \begin{aligned}\alpha' &= -\frac{P(\lambda + \mu)}{\mu(3\lambda + 2\mu)} = -\frac{P}{E}, \\ \beta &= \frac{P\lambda}{2\mu(3\lambda + 2\mu)} = \frac{P\sigma}{E},\end{aligned}\right\}$$

where  $E$  = Young's Modulus,  
 $\sigma$  = Poisson's Ratio.

The conclusion is that Young's Modulus is correctly given by (stress/strain), as is Poisson's Ratio by (lateral expansion/longitudinal contraction), provided  $\widehat{zz}$  is uniform and  $\widehat{rr}$  is independent of  $z$ . These two provisos mean that the end pressure must be uniformly distributed, and all the horizontal cross-sections (including the end faces) must expand equally. The conditions are invalidated by any form of end constraint. The insertion of cardboard, for example, between the face-plate and the specimen would introduce a frictional restraint if the cardboard failed to flow as readily as the specimen. On the other hand, sheet lead similarly inserted would have the opposite effect if it flowed more readily than did the specimen, thereby tending to compel the test piece to move overmuch. The tendency of an end constraint, either by friction or imbedding in the face plate, is to curve the plane end of the test piece, thereby destroying the uniformity of pressure distribution and creating high local stresses.



## SECTION III.

Since it is impossible to guarantee the complete absence of end restraints in a compression test, and since the presence of such restraints invalidates the experiment as a means of finding Young's Modulus, it remains to find what useful information can be derived from a compression test.

From a survey of equations (2), (3), and (6) it seems apparent that all the quantities (except the fundamental variables  $r, \theta, z$ ) should be expressible in terms of a single function. For theoretically  $\varpi_\theta$  is determined in terms of  $\Delta$  from equation (6), and equations (2) and (3) then determine  $u$  and  $w$  in terms of  $\Delta$  also. The actual results, which need not be deduced here, are given elsewhere\*. They are:

$$\begin{aligned}\widehat{r}r &= \frac{\partial}{\partial z} \left\{ \sigma \nabla^2 \chi - \frac{\partial^2 \chi}{\partial r^2} \right\}, & \widehat{r}z &= \frac{\partial}{\partial r} \left\{ (1-\sigma) \nabla^2 \chi - \frac{\partial^2 \chi}{\partial z^2} \right\}, \\ \theta\theta &= \frac{\partial}{\partial z} \left\{ \sigma \nabla^2 \chi - \frac{1}{r} \cdot \frac{\partial \chi}{\partial r} \right\}, & u &= -\frac{1+\sigma}{E} \cdot \frac{\partial^2 \chi}{\partial r \cdot \partial z}, \\ \widehat{z}z &= \frac{\partial}{\partial z} \left\{ (2-\sigma) \nabla^2 \chi - \frac{\partial^2 \chi}{\partial z^2} \right\}, & w &= \frac{1+\sigma}{E} \left\{ (1-2\sigma) \nabla^2 \chi + \frac{\partial^2 \chi}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial \chi}{\partial r} \right\} \\ & & &= \frac{1+\sigma}{E} \left\{ 2(1-\sigma) \nabla^2 \chi - \frac{\partial^2 \chi}{\partial z^2} \right\},\end{aligned}$$

where  $\sigma$  = Poisson's Ratio,  $E$  = Young's Modulus, and  $\nabla^2$  denotes Laplace's operator  $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ , and  $\chi$  satisfies the equation  $\nabla^4 \chi = 0$ . With regard to the operator  $\nabla^2$ , we note that in cylindrical coordinates it takes the form

$$\frac{1}{r} \cdot \frac{\partial}{\partial r} \left( r \cdot \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \cdot \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2},$$

and as we are at present concerned only with symmetrical displacements, the middle term of these three disappears. The operator therefore reduces to

$$\frac{1}{r} \cdot \frac{\partial}{\partial r} \left( r \cdot \frac{\partial}{\partial r} \right) + \frac{\partial^2}{\partial z^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}.$$

To determine suitable forms for  $\chi$  we note that every solution of  $\nabla^2 \chi = 0$  is necessarily a solution of  $\nabla^4 \chi = 0$ . The first step, therefore, is to determine suitable solutions of  $\nabla^2 \chi = 0$ . Accordingly we assume as a possible solution,

$$\chi = f(r) \cdot \phi(z).$$

\* Love, 'Mathematical Theory of Elasticity,' 3rd edit. p. 278.

The equation  $\nabla^2 \chi = 0$  then becomes

$$\frac{1}{r} \cdot \phi \cdot f' + \phi \cdot f'' + f \cdot \phi'' = 0,$$

or

$$\frac{f'' + \frac{1}{r} f'}{f} + \frac{\phi''}{\phi} = 0,$$

where primes denote differentiations. As the former term contains only  $r$  and the latter only  $z$ , we conclude that each is a constant, i. e.,

$$\frac{\phi''}{\phi} = k^2, \quad \text{or} \quad \phi'' - k^2 \phi = 0,$$

and

$$\frac{f'' + \frac{1}{r} f'}{f} = -k^2, \quad \text{or} \quad f'' + \frac{1}{r} f' + k^2 f = 0.$$

The former of these yields  $\phi = e^{\pm kz}$ , and the latter, on substituting  $t = kr$ , gives the Bessel equation of order zero. Its solution is therefore  $f = J_0(kr)$ , and the complete solution is

$$\chi = e^{\pm kz} \cdot J_0(kr),$$

where  $k$  is any constant.

Forms of  $\chi$  which satisfy  $\nabla^4 \chi = 0$  but not  $\nabla^2 \chi = 0$  can be found as follows. If  $\chi$  contains a parameter  $k$ , we have

$$\frac{\partial}{\partial k} \nabla^4 \chi = \nabla^4 \frac{\partial \chi}{\partial k} = 0,$$

which shows that  $\frac{\partial \chi}{\partial k}$  is a solution. Now

$$\begin{aligned} \frac{\partial}{\partial k} \{e^{kz} \cdot J_0(kr)\} &= z \cdot e^{kz} J_0(kr) + e^{kz} \cdot \frac{\partial J_0(kr)}{\partial r} \cdot \frac{\partial r}{\partial (kr)} \cdot \frac{\partial (kr)}{\partial k} \\ &= z \cdot e^{kz} J_0(kr) + \frac{r}{k} \cdot e^{kz} \cdot \frac{\partial}{\partial r} J_0(kr). \quad \dots (8) \end{aligned}$$

Also

$$\nabla^2 \left\{ r \cdot e^{kz} \frac{\partial}{\partial r} J_0(kr) \right\} = -2k^2 \cdot e^{kz} \cdot J_0(kr),$$

which proves that each term on the right of equation (8) is separately a solution of  $\nabla^4 \chi = 0$ . [Examination shows the former of these two to be of little value in the present investigation; we therefore confine ourselves to the latter of the two.]

Hitherto no restrictions have been placed on the constant  $k$ , which may be real or imaginary. If we take it as imaginary,

and remember that  $J_0(x) = J_0(-x)$ , we can add or subtract corresponding pairs of solutions, thus deducing solutions of the types

$$\frac{\sin}{\cos}(kz) \cdot I_0(kr), \quad r \frac{\sin}{\cos}(kz) \frac{\partial}{\partial r} I_0(kr),$$

where  $I_0$  is the modified Bessel function of the first kind. The modified Bessel functions of the second kind, the so-called K functions, are useless for our present purpose owing to their infinities on the axis. If we take the origin of coordinates at the middle of the axis of the cylinder, we see from equations (7) that  $\chi$  must be an odd function of  $z$  and an even function of  $r$ . We therefore reject the cosine terms and retain only solutions of the types

$$\chi_1 = \sin(kz) \cdot I_0(kr),$$

$$\chi_2 = r \cdot \sin(kz) \cdot \frac{\partial}{\partial r} I_0(kr) = r \cdot \sin(kz) \cdot I'_0(kr).$$

In addition to the foregoing periodic solutions we can find a finite polynomial solution. To be odd in  $z$  and even in  $r$ , it must have the form

$$\begin{aligned} \chi_3 = & a_1 z \\ & + a_3 z^3 + b_1 r^2 z \\ & + a_5 z^5 + b_3 r^2 z^3 + c_1 r^4 z \\ & + a_7 z^7 + b_5 r^2 z^5 + c_3 r^4 z^3 + d_1 r^6 z \\ & + \dots \\ & + \dots \end{aligned}$$

As this has to satisfy  $\nabla^4 \chi_3 = 0$ , there will be certain relations between these coefficients. The operator  $\nabla^4$ , written at length, is

$$\delta^4 + \frac{2}{r} \delta^3 - \frac{1}{r^2} \delta^2 + \frac{1}{r} \delta + 2\delta^2 D^2 + \frac{2}{r} \delta D^2 + D^4,$$

where

$$\delta = \frac{\partial}{\partial r}, \quad D = \frac{\partial}{\partial z},$$

and on evaluating  $\nabla^4 \chi_3$  it will be found that

(i.) terms of degree 1 and 3 satisfy identically,

(ii.) terms of degree 5 require

$$15a_5 + 6b_3 + 8c_1 = 0, \quad \dots \quad (9)$$

(iii.) terms of degree 7 require

$$105a_7 + 20b_5 + 8c_3 = 0, \quad \dots \quad (10)$$

$$\text{and} \quad 5b_5 + 8c_3 + 24d_1 = 0, \quad \dots \quad (11)$$

and so on. This can be continued to any desired degree.

As  $\chi_1$ ,  $\chi_2$ , and  $\chi_3$  are all solutions of  $\nabla^4 \chi = 0$ , it follows that  $A\chi_1 + B\chi_2 + \chi_3$  is also a solution, where A, B are any constants. The general solution can be written

$$\sum_{n=1}^{\infty} \{ A_n \sin(k_n z) I_0(k_n r) + B_n r \sin(k_n z) I_0'(k_n r) \} + \chi_3.$$

It remains to choose the A's, B's, and k's to satisfy given boundary conditions. To do this, it is an advantage to know the quota from  $\chi_1$ ,  $\chi_2$  to each of the quantities in equations (7). We find these, using primes to denote differentiations with respect to  $r$  and taking advantage of the relation

$$I_0''(kr) + \frac{1}{r} \cdot I_0'(kr) = k^2 I_0(kr).$$

We further abbreviate by omitting all arguments—which for the Bessel functions are  $(kr)$ , and for the trigonometrical functions are  $(kz)$ —and write S for  $\sin(kz)$ , C for  $\cos(kz)$ . The results, which can be easily verified, are tabulated here :—

	From $\chi_1$	From $\chi_2$
$\widehat{r}$ .....	$-kCI_0''$	$k^2 C \{ (2\sigma - 1) I_0 - r I_0' \}$
to $\widehat{\theta\theta}$ .....	$-kCI_0'/r$	$k^2 (2\sigma - 1) CI_0$
to $\widehat{z}$ .....	$k^2 CI_0$	$k^2 C \{ 2(2 - \sigma) I_0 + r I_0' \}$
to $\widehat{rz}$ .....	$k^2 SI_0'$	$k^2 S \{ k^2 r I_0 + 2(1 - \sigma) I_0' \}$
to $u$ .....	$-\frac{1+\sigma}{E} kCI_0'$	$-\frac{1+\sigma}{E} k^2 r CI_0$
to $w$ .....	$\frac{1+\sigma}{E} k^2 SI_0$	$\frac{1+\sigma}{E} \cdot k^2 S \{ 4(1 - \sigma) I_0 + r I_0' \}$

Probably the most likely condition to be attained in practice is that of keeping the ends of the test piece flat, especially if the face plates were very hard. We will proceed on this assumption. Analytically this will mean that  $w$  is independent of  $r$  when  $z=h$ , where  $2h$ =height of cylinder. The above table shows that  $w$  can be made independent of  $r$  provided (i.)  $\sin(kh)=0$ , (ii.)  $\chi_2$ 's quota to  $w$  is independent of  $r$ . The former proviso fixes the  $k$ 's, giving  $kh=n\pi$ , where  $n$  is an integer. The second proviso needs some examination.

If we use equations (7) to evaluate  $\chi_2$ 's quota to  $\frac{Ew}{1+\sigma}$ ,

we get, on the assumption that  $\chi_3$  stops at terms of degree 7, an expression of the form

$$L + Mr^2 + Nr^4,$$

where  $L$ ,  $M$ , and  $N$  are functions of  $z$ . To carry out the second of the aforementioned provisos we therefore require  $N=M=0$  when  $z=h$ . The work of evaluating  $M$  and  $N$  from the expression for  $\chi_3$  yields

$$(1-2\sigma)c_3 + 12(1-\sigma)d_1 = 0 \quad \dots \quad (12)$$

and 
$$(1-2\sigma)(3b_3 + 10b_5h^2) + 16(1-\sigma)(c_1 + c_3h^2) = 0. \quad (13)$$

We now make  $\widehat{rz}$  vanish over the curved surface, *i. e.* when  $r=a$ , where " $a$ " is the radius of the test piece. A glance at the tabulated results shows that the quota from  $\chi_1$ ,  $\chi_3$  to  $\widehat{rz}$  vanish identically when  $z=h$ , since  $\sin(kh) \equiv 0$ . It follows that  $\chi_3$ 's quota to  $\widehat{rz}$  must vanish in similar circumstances, *i. e.*, when  $r=a$  and  $z=h$ . The actual evaluation of  $\chi_3$ 's quota to  $\widehat{rz}$  yields as an equation of condition,

$$(1-\sigma)(8c_1 + 8c_3h^2 + 36a^2d_1) = \sigma(3b_3 + 6c_3a^2 + 10b_5h^2). \quad (14)$$

The last six equations (9) to (14) inclusive enable us to express the six variables  $a_7$ ,  $a_5$ ,  $b_5$ ,  $b_3$ ,  $c_3$ , and  $c_1$  in terms of  $d_1$ . On solving them we get

$$\begin{aligned} a_7 &= -\frac{32}{35}d_1 \frac{2-\sigma}{1-2\sigma}, & a_5 &= \frac{-4d_1}{5(1-2\sigma)} \{8h^2(\sigma-2) + 3a^2(3-2\sigma)\}, \\ b_5 &= \frac{24}{5}d_1 \frac{3-2\sigma}{1-2\sigma}, & b_3 &= \frac{8d_1}{(1-2\sigma)} \{2h^2(2\sigma-3) + 3a^2(1-\sigma)\}, \\ c_3 &= -12d_1 \frac{1-\sigma}{1-2\sigma}, & c_1 &= \frac{3d_1}{2(1-2\sigma)} \{8h^2(1-\sigma) - 3a^2(1-2\sigma)\}. \end{aligned}$$

As  $\chi_3$ 's quota to  $\widehat{rz}$  is found to be actually

$$4rz[(1-\sigma)(8c_1 + 8c_3z^2 + 36r^2d_1) - \sigma(6c_3r^2 + 3b_3 + 10b_5z^2)],$$

it reduces at the curved surface  $r=a$  to

$$192ad_1z(h^2 - z^2)(2-\sigma)/(1-2\sigma).$$

In this the  $z$  and  $z^3$  can be replaced by series of sines of multiples of  $(\pi z/h)$  by the relations

$$\begin{aligned} z &= \sum_1^{\infty} (-1)^{n-1} \frac{2h}{n\pi} \sin \frac{n\pi z}{h}, \\ z^3 &= \sum_1^{\infty} (-1)^{n-1} \left( \frac{2h^3}{n\pi} - \frac{12h^3}{n^3\pi^3} \right) \sin \frac{n\pi z}{h}. \end{aligned}$$

The value of  $\widehat{rz}$ , as determined from the general solution given at the top of p. 471, can now be expressed as a series of sines of multiples of  $(\pi z/h)$ . Consequently  $\widehat{rz}$  vanishes over the curved surface if the coefficient of each sine vanishes separately. As coefficient of  $\sin(n\pi z/h)$  we have

$$A_n k_n^2 I_0'(k_n a) + B_n k_n^2 \{k_n^2 a I_0(k_n') + 2(1-\sigma) I_0'(k_n a)\} \\ + 192ad_1 \frac{(2-\sigma)}{(1-2\sigma)} \frac{12h^3}{n^3 \pi^3} (-1)^{n-1} = 0, \quad (15)$$

which gives one relation between  $A_n$  and  $B_n$ .

We now make  $\widehat{rr}$  vanish over the curved surface. The quota from  $\chi_3$  to  $\widehat{rr}$ , when evaluated for  $r=a$ , is of the form  $L + Mz^2 + Nz^4$ , where

$$L = 2b_1(2\sigma-1) + 6\sigma a_3 + \frac{12ad_1}{(1-2\sigma)} \{a^2(2-\sigma) - 4h^2(3-\sigma)\},$$

$$M = \frac{144d_1}{(1-2\sigma)} \{a^2(2-\sigma) + 2h^2\}, \quad N = -\frac{144d_1}{(1-2\sigma)}.$$

For the  $z$  and  $z^4$  terms we can substitute series of cosines from the relations

$$z^2 = \frac{h^2}{3} + \sum_{n=1}^{\infty} \left(\frac{2h}{n\pi}\right)^2 (-1)^n \cos \frac{n\pi z}{h},$$

$$z^4 = \frac{h^4}{5} + \sum_{n=1}^{\infty} 8h^4 (-1)^n \left(\frac{1}{n^2 \pi^2} - \frac{6}{n^4 \pi^4}\right) \cos \frac{n\pi z}{h}.$$

The value of  $\widehat{rr}$  (at  $r=a$ ) as determined from the general solution on p. 471 can be expressed as an independent term plus a series of cosines of multiples of  $(\pi z/h)$ ; for  $\chi_1$  and  $\chi_3$  contribute cosines, *vide* table on p. 471. Consequently we can make  $\widehat{rr}$  vanish over the curved surface if we equate the independent term and the coefficient of each cosine separately to zero. The latter gives

$$-A_n \cdot \frac{n\pi}{h} I_0''\left(\frac{n\pi a}{h}\right) \\ + B_n \left(\frac{n\pi}{h}\right)^3 \left\{ (2\sigma-1) I_0\left(\frac{n\pi a}{h}\right) - a I_0'\left(\frac{n\pi a}{h}\right) \right\} \\ + \frac{144}{(1-2\sigma)} \cdot \frac{4h^2 d}{n^2 \pi^2} \cdot (-1)^n \left\{ \frac{12h}{n^2 \pi^2} + a^2(2-\sigma) \right\} = 0, \\ \dots \quad (16)$$

which, with equation (15) *supra*, serves to determine the  $A$ 's

474 Mr. F. E. Relton on the Determination of Young's and B's. The independent term gives

$$L + \frac{1}{3}Mh^2 + \frac{1}{3}Nh^4 = 0,$$

or

$$b_1(1-2\sigma) - 3a_3\sigma = \frac{6d_1}{(1-2\sigma)} \{a^4(2-\sigma) - 4a^2h^2 + \frac{8}{5}h^4\}. \quad (17)$$

We now have to make the total end load equal to a given quantity, i. e.,

$$-\pi a^2 Q = \iint \widehat{zz} \cdot r \cdot d\theta \cdot dr,$$

or

$$-\frac{a^2 Q}{2} = \int_0^a \widehat{zz} \cdot r \cdot dr,$$

where Q=average load per unit area. In order to effect this integration it is convenient to take  $\widehat{zz}$  in parts. The quota to  $\widehat{zz}$  from  $\chi_3$  becomes, when  $z=h$ ,

$$4b_1(2-\sigma) + 6a_3(1-\sigma) + \frac{12d_1}{(1-2\sigma)} \{12a^2h^2(1-\sigma) - 8h^4(2-\sigma) + 6a^2r^2\sigma - 16h^2r^2(1-\sigma) - 3r^4\sigma\}.$$

If we substitute this in the integral  $\int_0^a \widehat{zz} \cdot r \cdot dr$  and evaluate, we get

$$a^2 \{2b_1(2-\sigma) + 3a_3(1-\sigma)\} + \frac{12a^2d_1}{(1-2\sigma)} \{a^4\sigma + 2a^2h^2(1-\sigma) - 4h^4(2-\sigma)\}.$$

The quota to  $\widehat{zz}$  from  $A\chi_1 + B\chi_2$  can be written in brief as

$$k^3 C [A I_0 + B \{2(2-\sigma) I_0 + r I_0'\}].$$

We substitute this in  $\int_0^a \widehat{zz} \cdot r \cdot dr$  and evaluate, i. e.,

$$k^3 C \int_0^a [\{A + 2B(2-\sigma)\} I_0 r + B r^2 I_0'] \cdot dr.$$

Now

$$\int r^2 I_0' \cdot dr = r^2 I_0 - 2 \int r I_0 \cdot dr,$$

so that the above integral becomes

$$k^3 C \int_0^a \{A + 2B(1-\sigma)\} I_0 \cdot r \cdot dr + B k^3 a C I_0(ka).$$

Also, from the relation

$$I_0'' + \frac{1}{r} I_0' = k^2 I_0,$$

we have

$$\int r \cdot I_0'' \cdot dr + \int I_0' \cdot dr = k^2 \int r \cdot I_0 \cdot dr;$$

whence  $\int_0^a [r I_0'] = k^2 \int_0^a r I_0 \cdot dr$ ,

so that the above integral becomes

$$kaC[AI_0' + B\{2(1-\sigma)I_0' + ak^2I_0\}].$$

The value of this is given by equation (15).

When  $\hat{z}$  is determined from the more general value  $\sum_{n=1}^{\infty} (A\chi_1 + B\chi_2)$ , the integral

$$\int_0^a \hat{z} \cdot r \cdot dr = 12.192a^2d_1 \frac{(2-\sigma)}{(1-2\sigma)} \cdot \frac{h^4}{\pi^4} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^4} \cos \frac{(n\pi z)}{h},$$

when  $z=h$ .

Using

$$\sum_{n=1}^{\infty} (-1)^n n^{-4} \cdot \cos \left( \frac{n\pi z}{h} \right) = -\pi^4 \left\{ \frac{z^4}{48h^4} - \frac{z^2}{24h^2} + \frac{7}{720} \right\}$$

$$= \frac{\pi^4}{90}, \text{ when } z=h,$$

the above reduces to  $\frac{128}{5} \cdot h^4 a^2 d_1 \frac{(2-\sigma)}{(1-2\sigma)}$ . The equation for the end pressure,  $Q$ , therefore gives ultimately

$$-\frac{Q}{2} = 2b_1(2-\sigma) + 3a_2(1-\sigma) + \frac{12d_1}{(1-2\sigma)} \left\{ a^4\sigma + 2a^2h^2(1-\sigma) - \frac{28}{15}h^4(2-\sigma) \right\} \dots \dots (18)$$

At this stage of the work the position is as follows. There are five unknown quantities, viz.  $E$ ,  $\sigma$ ,  $a_2$ ,  $b_1$ , and  $d_1$ ; there are only two relations, viz. (17) and (18). The determination of  $E$  is inextricably bound up with  $\sigma$ . At least one physical measurement will have to be made, so that there are three courses open to us for the determination of the necessary three further relations. We can make

- (i) one measurement and two assumptions,
- or (ii) two measurements and one assumption,
- or (iii) three measurements.

This last course, though theoretically sound and on general grounds the most preferable, is beset with considerable difficulties, both Mechanical and Mathematical\*. If we make the assumption that  $\sigma$  may be treated as a known quantity, we are left with the option of making

- (i) one measurement and one further assumption,
- or (ii) two measurements.

\* It is hoped to explore this avenue in a future paper.



The one further assumption that recommends itself is to suppose there is no movement at the face-plate, *i. e.*, that the periphery of the end face does not move\*. This would be difficult, if not impossible, to ensure in practice and we choose the alternative of making two measurements, which would be (i.) the contraction of a measured axial length, and (ii.) the extension of the diameter of the middle cross-section (*i. e.*, the value of  $u$  when  $z=0$ ). These two measurements could be made by using longitudinal and lateral extensometers simultaneously.

We proceed to the second of the two measurements, the value of  $u$  when  $z=0$  and  $r=a$ . The quota from  $\chi_3$  to  $-\frac{Eu}{1+\sigma}$  is

$$\frac{\partial^2 \chi_3}{\partial r \cdot \partial z} = 2b_1 r + 6b_3 r z^2 + 4c_1 r^3 + 10b_5 r z^4 + 12c_3 r^3 z^2 + 6d_1 r^5.$$

When  $r=a$  and  $z=0$ , this evaluates to

$$2ab_1 - 12a^5 d_1 + 48a^3 h^2 d_1 \frac{(1-\sigma)}{(1-2\sigma)} - 48ah^4 d_1 \frac{(3-2\sigma)}{(1-2\sigma)}.$$

The quota from  $A\chi_1 + B\chi_2$  can be determined thus. Its value, from p. 471, is  $AkCI_0' + Bk^3(aI_0)$ . If we put

$$AI_0' + Bk^2 a I_0 + \phi = 0, \quad . \quad . \quad . \quad (19)$$

where the argument of the Bessel functions is  $ka$ , we have from (15), (16), and (19), by eliminating  $A$ ,  $B$  the relation :

$$\begin{vmatrix} I_0', & ak^2 I_0 + 2(1-\sigma)I_0', & 4ak^{-2}H(2-\sigma) \\ I_0'', & ak^2 I_0' + k^2(1-2\sigma)I_0, & \{12k^{-2} + a^2(2-\sigma)\}H \\ I_0, & k^2 a I_0, & \phi \end{vmatrix} = 0,$$

where

$$H = \frac{12.484d_1}{(1-2\sigma)k^3}(-1)^{n-1},$$

whence

$$\begin{aligned} \frac{\phi}{H} &= 4ak^{-2}(2-\sigma) \\ &+ 2(1-\sigma) \frac{I_0' [I_0' \{a^2(2-\sigma) + 4k^{-2}(5-\sigma)\} - 4a(2-\sigma)I_0]}{ak^4 I_0^2 - I_0'^2 \{ak^2 + 2(1-\sigma)a^{-1}\}}. \end{aligned}$$

The quota from the more general value  $\Sigma(A\chi_1 + B\chi_2)$  is therefore  $-\Sigma k\phi \cos(n\pi z/h)$ , which falls into two parts

\* This is the assumption made in Filon's paper, *l. c.*

from the known value of  $\phi$  above. The first part gives  $-\sum 4ak^{-1}H(2-\sigma)\cos\pi z/h$ , which, when  $z=0$ , reduces to  $-\frac{112}{5}ah^4d_1\frac{(2-\sigma)}{(1-2\sigma)}$ . The second part gives

$$+24.48ad_1\frac{(1-\sigma)}{(1-2\sigma)}\sum\frac{I_0'[I_0'\{a^2(2-\sigma)+4k^{-2}(5-\sigma)\}-4a(2-\sigma)I_0]}{k^2[a^2k^4I_0^2-I_0'^2\{a^2k^2+2(1-\sigma)\}]}(-1)^n.$$

Since

$$I_0'(kr) = \frac{\partial}{\partial r} I_0(kr) = kI_1(kr),$$

we deduce that the value of  $u$  when  $z=0$ ,  $r=a$  is

$$\begin{aligned} & -\frac{1+\sigma}{E}\left[2ab_1-12a^5d_1+48a^3h^2d_1\frac{(1-\sigma)}{(1-2\sigma)}-\frac{16}{5}ah^4d_1\frac{(59-37\sigma)}{(1-2\sigma)}\right. \\ & \left.+24.48ad_1\frac{(1-\sigma)}{(1-2\sigma)}\sum\frac{I_1^2\{a^2k^2(2-\sigma)+4(5-\sigma)\}-4ak(2-\sigma)I_0I_1}{k^4[a^2k^2(I_0^2-I_1^2)-2I_1^2(1-\sigma)]}(-1)^n\right]. \end{aligned} \quad (20)$$

In a similar manner we now determine the former of the two measurements, i. e., the contraction of an axial length,  $l$ , say. The quota from  $\chi_3$  to  $w$  is given by

$$\begin{aligned} \frac{Ew}{(1+\sigma)} &= 8b_1z(1-\sigma)+6a_3z(1-2\sigma)+20a_5z^3(1-2\sigma) \\ &+ 8b_3z^3(1-\sigma)+8b_5z^5(1-\sigma)+42a_7z^5(1-2\sigma) \\ &+ r^2[32c_1z(1-\sigma)+6b_3z(1-2\sigma)+32c_3z^3(1-\sigma) \\ &+ 20b_5z^3(1-2\sigma)] \\ &+ r^4[72d_1z(1-\sigma)+6c_3z(1-2\sigma)]. \end{aligned}$$

If we compute this for  $r=a$ ,  $z=l$ , it yields

$$\begin{aligned} & 2l\{4b_1(1-\sigma)+3a_3(1-2\sigma)\} \\ & -\frac{48a^2d_1l^3}{1-2\sigma}-\frac{128d_1h^2l^3}{1-2\sigma}+\frac{96a^2h^2d_1l}{1-2\sigma}+\frac{192d_1l^5}{5(1-2\sigma)}. \end{aligned}$$

The quota to  $Ew/(1+\sigma)$  from  $A\chi_1+B\chi_3$  is

$$k^2S[AI_0+B\{4(1-\sigma)I_0+aI_0'\}].$$

Put

$$AI_0+B\{4(1-\sigma)I_0+aI_0'\}+\theta=0,$$

so that, as for the determination of  $\phi$ , we get

$$\begin{vmatrix} I_0', & ak^2I_0+2(1-\sigma)I_0', & 4ak^{-2}H(2-\sigma) \\ I_0'', & ak^2I_0'-k^2(2\sigma-1)I_0, & \{12k^{-2}+a^2(2-\sigma)\}H \\ I_0, & 4(1-\sigma)I_0+aI_0', & \theta \end{vmatrix} = 0,$$

whence

$$\frac{\theta}{H} = k^{-4} \{ 4(2\sigma^2 - 7\sigma + 9) + a^2 k^2 (2 - \sigma) \} \\ I_0 \{ 8(7 - 2\sigma) k^{-2} + 2a^2 (2 - \sigma) \} - I_0' \{ 10a(2 - \sigma) k^{-2} \\ + 8(2\sigma^2 - 7\sigma + 9) a^{-1} k^{-4} \} \\ - (1 - \sigma) I_0' \cdot \frac{ak^4 I_0^2 - I_0'^2 \{ ak^2 + 2(1 - \sigma) a^{-1} \}}{ak^4 I_0^2 - I_0'^2 \{ ak^2 + 2(1 - \sigma) a^{-1} \}}.$$

The quota from the more general value  $\Sigma (A\chi_1 + B\chi_2)$  is therefore  $-\Sigma k^2 \theta \sin(kl)$ , which falls into two parts from the known value of  $\theta$  above. The first part gives

$$12.48d_1(1 - 2\sigma)^{-1} [4(2\sigma^2 - 7\sigma + 9)k^{-5} \\ + a^2(2 - \sigma)k^{-3}] (-1)^n \sin(kl).$$

As

$$\Sigma \frac{(-1)^n}{k^3} \sin(kl) = \left(\frac{h}{\pi}\right)^3 \Sigma \frac{(-1)^n}{n^3} \sin\left(\frac{n\pi l}{h}\right) = \frac{l(l^2 - h^2)}{12}$$

and

$$\Sigma \frac{(-1)^n}{k^5} \sin(kl) = \left(\frac{h}{\pi}\right)^5 \Sigma \frac{(-1)^n}{n^5} \sin\left(\frac{n\pi l}{h}\right) \\ = -\frac{l}{24} \left( \frac{7h^4}{30} - \frac{h^2 l^2}{3} + \frac{l^4}{10} \right),$$

this first part would give

$$-\frac{12.48d_1 l}{(1 - 2\sigma)} \left[ \frac{(2\sigma^2 - 7\sigma + 9)}{6} \left( \frac{7h^4}{30} - \frac{h^2 l^2}{3} + \frac{l^4}{10} \right) + \frac{a^2(2 - \sigma)(h^2 - l^2)}{12} \right].$$

It may be shown, too, that the second part would give on reduction :

$$12.48ad_1 \frac{(1 - \sigma)}{(1 - 2\sigma)} \Sigma \frac{I_0 I_1 \{ 8(7 - 2\sigma) + 2a^2 k^2 (2 - \sigma) \} - I_1^2 \{ 10ak(2 - \sigma) \\ + 8(2\sigma^2 - 7\sigma + 9)/ak \}}{k^4 \{ a^2 k^2 (I_0^2 - I_1^2) - 2(1 - \sigma) I_1^2 \}} \\ \times (-1)^{n-1} \sin(kl) \\ = Md_1, \text{ say.}$$

The actual value of  $\frac{Ew}{(1 + \sigma)}$  is therefore

$$2l \{ 4b_1(1 - \sigma) + 3a_3(1 - 2\sigma) \} \\ + Md_1 + \frac{16d_1 l}{(1 - 2\sigma)} \left[ 3a^2 h^2 \sigma + 3(1 - \sigma) a^2 l^2 + 2(1 - \sigma)(5 - 2\sigma) h^2 l^2 \right. \\ \left. - \frac{7h^4}{5} (2\sigma^2 - 7\sigma + 9) - \frac{3l^4}{5} (2\sigma^2 - 7\sigma - 11) \right]. \quad (21)$$

We are now in possession of the necessary four relations, viz. (17), (18), (20), and (21), and since the quantities

( $h/a$ ), ( $l/a$ ) are purely numerical, as is  $ak$ , we may re-write these relations in the forms :

$$b_1(1-2\sigma) - 3a_3\sigma - Aa^4d_1(1-2\sigma)^{-1} = 0, \quad . \quad . \quad (17a)$$

$$2b_1(2-\sigma) + 3a_3(1-\sigma) - Ba^4d_1(1-2\sigma)^{-1} + Q/2 = 0, \quad . \quad . \quad (18a)$$

$$2b_1 - Ca^4d_1(1-2\sigma)^{-1} + Eu/(1+\sigma)a = 0, \quad . \quad . \quad (20a)$$

$$8b_1(1-\sigma) + 6a_3(1-2\sigma) - Da^4d_1(1-2\sigma)^{-1} + Ew/(1+\sigma)l = 0, \quad . \quad . \quad (21a)$$

where A, B, C, and D are somewhat complicated but purely numerical coefficients. These permit of the elimination of  $a_3$ ,  $b_1$ , and  $a^4d_1/(1-2\sigma)$ .

When the eliminant is written down in determinant form, the elements of the last column are

$$0, \quad \frac{Q}{2}, \quad \frac{Eu}{a(1+\sigma)}, \quad \text{and} \quad \frac{Ew}{l(1+\sigma)}.$$

If each of these be divided by the last named, they become

$$0, \quad \frac{(1+\sigma)}{2} \cdot \frac{Ql}{Ew}, \quad \frac{lu}{aw}, \quad \text{and} \quad 1.$$

Now  $Ql/w$  is the value of E as determined by the experiment; let us denote it by  $E'$ . Further, ( $lu/aw$ ) is the value of  $\sigma$  as determined by experiment; let us denote it by  $\sigma'$ . The element of the last column can now be written

$$0, \quad \frac{(1+\sigma)}{2} \cdot \frac{E'}{E}, \quad \sigma', \quad \text{and} \quad 1.$$

The eliminant is therefore

$$\begin{vmatrix} (1-2\sigma), & -3\sigma, & A, & 0 \\ 4-2\sigma, & 3-3\sigma, & B, & \frac{1+\sigma}{2} \cdot \frac{E'}{E} \\ 2, & 0, & C, & \sigma' \\ 8(1-\sigma), & 6(1-2\sigma), & D, & 1 \end{vmatrix} = 0,$$

which can be written in various forms, of which the neatest is probably

$$\left(\frac{E'}{E} - 1\right) \{2A(1-2\sigma) + D\sigma - C\} = (\sigma' - \sigma) \left\{ D - 2 \cdot \frac{2A\sigma + B}{(1+\sigma)} \right\}. \quad (22)$$

This relation has some intriguing and even arresting consequences. We notice that, of the two relations  $E = E'$ ,  $\sigma = \sigma'$ , each is a necessary consequence of the other, which means that the simultaneous experimental determination of Young's Modulus and Poisson's Ratio gives results which are either both correct or both incorrect. Each of the quantities  $E'$ ,  $\sigma'$  is variable with  $Q$  but they are connected by a linear relation, so that if various experimental values are determined for different values of  $Q$  the plotted results should lie on a straight line. This straight line does not, in general, pass through the origin, though it does pass through the point  $(E, \sigma)$ . Slight and erratic departures from collinearity in the plotted observations would be attributable to experimental errors, but systematic variations would indicate that the material under test was anisotropic.

The quantities on which observations would be made are  $Q$ ,  $u$ , and  $w$ . The equations (17a) to (21a) show that these three are connected by a linear relation; but there is no definitive relation between any two of these independent of the third, though in a general way they will all increase together. There is no simple connexion between  $Q$  and  $w$ , and the stress-strain relation of an isotropic material, when exhibited graphically, may quite well show erratic departures from the straight line. Such departures would naturally be attributed to errors of observation: in reality, they may be nothing of the sort. In the same way, a stress-strain relation that is slightly curved instead of being perfectly straight is no guarantee that the material does not obey Hooke's law.

The fact that, observational errors apart, the quantities  $E'$ ,  $\sigma'$  for an isotropic material are connected by a linear relation indicates a method of determining  $E$ ,  $\sigma$  more accurately if ever the need for such determination arises. The orientation of the line depends on the constants  $A$ ,  $B$ ,  $C$ ,  $D$ , and therefore on  $a$ ,  $h$ , and  $l$ , i. e. on the dimensions of the test piece and the length whose contraction is measured. Two sets of observations carried out without maintaining the ratios  $a:h:l$  would suffice. Alternatively, if a torsion test were considered reliable, a second linear relation is given by the connexion  $E = 2\mu(1 + \sigma)$ .

It is of interest to examine the reliability of the ordinary method of determining Young's Modulus. Filon has shown\* that, *ceteris paribus*, there is less error to be expected from long specimens than from short ones. He has computed that, for a material of uniconstant isotropy, a very short

\* *Loc. cit.*

specimen gives an error that approaches 20 per cent., on the assumption that there is no movement of the periphery of the end face. In the present paper we have abandoned this assumption, so that it is not possible to present exactly analogous figures; but other illustrative results are given below.

There appears to be no standard practice in the matter of compression tests, but in certain cases it is held to be good practice to have the test piece half as long again as the diameter, and to measure over a length equal to the diameter, i. e.,  $a=l=2h/3$ .

In order to facilitate the computation of the I-functions, I have slightly modified these dimensions by taking  $a=l=2h/\pi$ . The values of A, B, etc. vary with  $\sigma$  as shown in the table:—

$\sigma$ .	A.	B.	C.	D.
0.2 .....	156.142	195.697	975.561	269.701
0.25.....	155.842	191.239	940.310	270.806
0.3 .....	155.542	186.780	905.115	271.722
0.35.....	155.242	182.324	869.994	272.518
0.4 .....	154.942	177.870	834.919	273.277

The corresponding forms of equation (22) are :

$$\left(\frac{E'}{E} - 1\right) = (\sigma' - \sigma) \times \begin{matrix} 0.2066 & \text{when } \sigma = 0.2 \\ 0.2170 & \\ 0.2275 & \\ 0.2344 & \\ 0.2379 & \end{matrix} \begin{matrix} \\ 0.25 \\ 0.3 \\ 0.35 \\ 0.4 \end{matrix}$$

It follows that, in general, the percentage error in the determination of E is about 20 per cent. of the actual error in the determination of  $\sigma$ , so that it may easily nullify the refinements of the compressometer. The experimental conditions under which the foregoing analysis is valid are probably best achieved by the three-piece method due to Prof. Coker\*.

In conclusion, the arithmetical work contained herein has been done several times *de novo* and I have every hope that it is correct, at least to the number of places given.

\* Journal of the Franklin Institute, vol. 196 No. 4, p. 447 (Oct. 1923).

XXXVIII. *On Gas Flow and Pressure Changes in Gases under Electric Discharge.* By R. G. LUNNON, M.A., M.Sc., *Armstrong College, Newcastle-upon-Tyne* \*.

THE experiments here recorded were made to measure the viscosity of gases whilst an electric discharge is passing through them. On the theoretical side the problem is a very complicated one, but it appears to merit examination, because of the possibility that, while the excited atoms are radiating energy, their electron orbits may be enlarged, and the consequent increase in the effective size of the atom may tend to reduce the viscosity. We found no evidence of such change: it is probably too small for measurement, by reason of the small number of excited atoms.

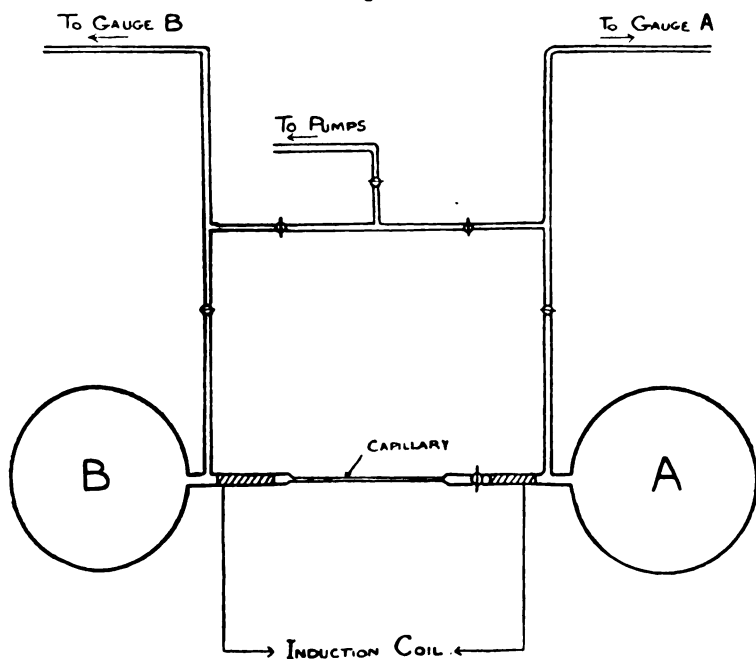
I.

On the experimental side the outstanding difficulty of the measurements lies in the disappearance and in the emission of gas during the discharge. So long as this occurs, the records of the pressure changes are no guide to the amount of gas flow through the capillary tube. In the first form of our apparatus the discharge tube was formed by two flasks connected by a fine capillary, and a McLeod gauge was connected to only one of the flasks; it was therefore impossible to check whether the total amount of gas remained constant. A second gauge was added, and revealed that both absorption and emission of gas occurred. No glass taps had been used, and mercury seals were used to control the flow. As the glow of the discharge passed over this mercury some oxidation occurred, and the seals were therefore replaced by taps. The gas continued to disappear, and the platinum-wire electrodes were next removed and replaced by large external electrodes of tinfoil wrapped round the tubes in the way described by Manley. The final form of the apparatus is shown in fig. 1. A, B are two bulbs of about 500 c.c. capacity, and some  $P_2O_5$  is kept in a small bulb attached to each. They are connected by a fine capillary tube C, 4.10 cm. long and 0.0791 mm. internal diameter; two other tubes were also used. The discharge occurred in A, B, and C, and the pressures in A and B were measured before and after a time of flow through C by connecting each bulb with its gauge. The relative volumes of bulb and gauge were known, and the proper allowance was made for the pressure in the gauge before connexion was made with its bulb.

\* Communicated by the Author.

Much attention has been given to the problems of the changes in gas-pressure, but the process has not yet been followed in the way which this apparatus permits. We have therefore made a number of measurements with gas-pressures from 0.01 mm. to 5.0 mm., and with currents of from 5 to 40 milliamperes, running from an induction coil for many hours at a time. It was found that the pressure

Fig. 1.

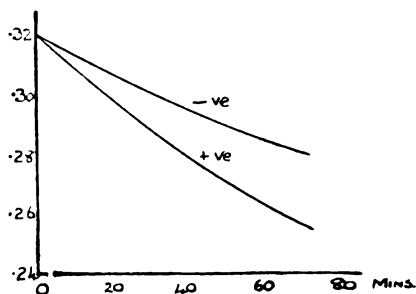
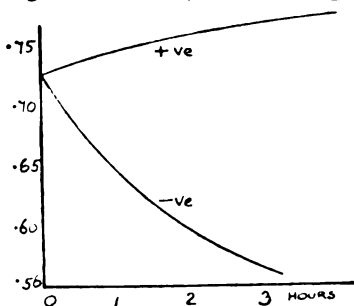
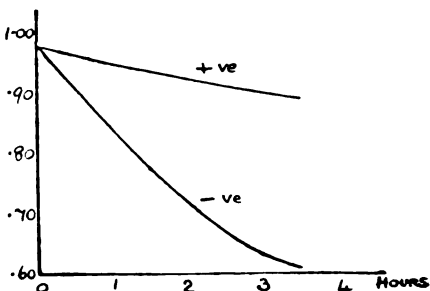
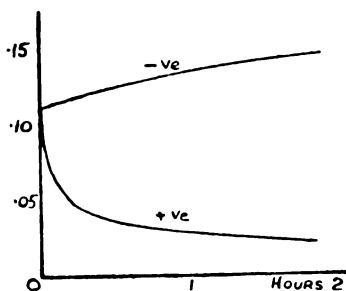
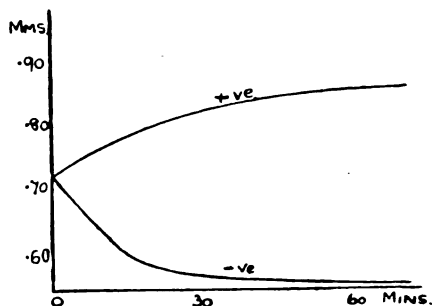
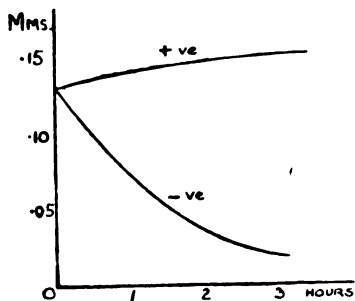


sometimes rose on the cathode side, sometimes fell ; often it fell on both sides, and sometimes it remained constant. Examples of these changes are given in the small graphs in fig. 2. The changes are found to follow in every case an exponential law ; some we have tested were records for every 30 minutes during 12 hours' discharge. When an increase of pressure occurred on one side, it tended to a maximum value ; when gas disappeared, on the other hand, a minimum was never reached, because the pressure became so low that the discharge ceased. The current was kept roughly constant during each experiment by frequent adjustment of the primary resistance. It is possible to calculate, from the data



given later, how much gas has flowed from one side to the other during these experiments; but the flow is very slow indeed, and the correction does not affect the general form of the curves shown.

Fig. 2.



Absorption of gas was especially marked if there was a trace of solid impurity in the tube. It occurred sometimes when the tube had been very carefully cleaned, and the gas was in contact only with the glass, with a very little tap-grease and with  $P_2O_5$  (the whole apparatus was made of glass). It was very much reduced when outside electrodes were introduced, and in the final apparatus it occurred on an average during only one-quarter of all the observed discharge

periods. (It has been recorded by Hill \* that gas disappears even during an electrodeless discharge, but in his experiments the current passed for a shorter time, and it is probable that the glass reaction was not then complete; some of the present discharge lasted for more than 20 hours, exclusive of intervals.) There was no obvious cause for the change when a period of absorption occurred. The only factor not completely examined was the character of the current from the induction coil; the amount of the current was kept constant, but there were appreciable variations in the character of the make and break of the coil, and the voltage across the tube was not constant. Final cases of absorption were most common with oxygen, which suggests chemical action.

## II.

The flow experiments were made with four different gases—chemically pure nitrogen, commercial oxygen, air, and a mixture of 75 per cent. argon with 25 per cent. nitrogen and a trace of oxygen. The whole apparatus was exhausted, using a mercury-vapour pump, before each gas was introduced. The main bulbs were so mounted that they could be surrounded by an electric furnace and maintained at 300° C. during evacuation. Pure phosphorus pentoxide, occasionally renewed, was kept in the apparatus throughout the experiments. In order that the discharge could pass, the pressures were within the limits 0.01 mm. and 2.0 mm. of mercury. Readings of the pressures were taken at intervals of half an hour or an hour, sometimes alternating periods of flow during discharge with periods of ordinary flow, and at other times taking longer periods of the two kinds of flow. Except when absorption or emission of gas occurred, there was no difference between the rates of flow in the two cases within less than .5 per cent. A typical set of readings for each of three gases is shown in the tables. In every case the pressures before and after the flow on each side of the capillary were read, and when slight differences occurred between the two changes of pressure (after allowing for the relative volumes of the two flasks) the mean was taken: when the differences were large, absorption had occurred, and the readings were rejected. In each set the mean pressure is approximately the same throughout, and therefore the “conductance” of the tube, Knudsen’s “T” (see below), should be constant whether the flow be viscous or molecular. Its apparently excellent constancy in the

\* Hill, *Proc. Phys. Soc.* xxv. 1912, p. 35.

oxygen set is fortuitous, for the pressure changes at the end of the set are so small that an error of 5 per cent. is possible. It is clear from the tables that the electric discharge has no effect upon the flow, whatever its direction; it is marked +ve when the positive electrode is on the side of higher pressure.

The pressures  $p_1, p_2$  are the initial pressures in the two bulbs;  $p_1', p_2'$  are the pressures after time  $t$ . The figures in the last column are proportional to the "conductance," and are obtained by dividing  $p_1 - p_1'$  by the time in minutes and by the mean difference of pressure,  $\frac{1}{2}(p_1 + p_1') - \frac{1}{2}(p_2 + p_2')$ .

$p_1$ mm. Hg.	$p_1'$ mm. Hg.	$p_2$ mm. Hg.	$p_2'$ mm. Hg.	$t$ minutes.	Current.	T.
<i>Air.</i>						
0.730	.702	0.027	.046	42	none	88. $10^{-4}$
.702	.670	.047	.072	56	+ve	88 "
.670	.649	.072	.090	45	none	81 "
.649	.628	.098	.115	51	-ve	75 "
.628	.599	.140	.165	82	none	77 "
.597	.548	.163	.150	32	+ve	absorption

*Argon and Nitrogen.*

.982	.944	.126	.160	92	none	50. $10^{-4}$
.750	.714	.122	.152	120	+ve	49 "
.714	.681	.152	.181	120	-ve	53 "
.645	.627	.202	.216	75	none	54 "
.604	.584	.216	.232	100	-ve	52 "
.584	.557	.231	.253	150	+ve	53 "
.560 *	.549	.254	.263	70	none	51 "

*Oxygen.*

1.931	1.780	.892	1.921	200	none	83. $10^{-4}$
1.803	1.698	1.019	1.108	180	+ve	84 "
1.662	1.570	1.091	1.095	120	+ve	absorption
1.567	1.350	1.094	1.112	300	-ve	"
1.352	1.312	1.107	1.141	220	none	88. $10^{-4}$
1.287	1.266	1.144	1.160	180	-ve	92 "
1.262	1.250	1.165	1.175	160	none	87 "

Current ..... Between 6 and 10 milliamperes in each case.  
 Volumes .....  $V_1$ : 394 c.c.;  $V_2$ : 504 c.c.  
 Temperature ...  $18^\circ \text{C}$ .

\* The composition of the argon mixture was slightly changed towards the end of this set of consecutive periods, because of the different rates of flow of argon and of nitrogen.

### III.

At the pressures which we have used, the coefficient of viscosity changes rapidly with pressure under normal conditions, and the term becomes meaningless at the lowest pressures. As the published data in this region are few, and there are none at all for mixtures other than air, we have recorded these results in full.

The usual expressions for the quantity of gas,  $Q$ , flowing through a capillary tube in one second, in terms of the mean pressure  $p$  between its ends, are these :

$$T = \frac{Q}{p_1 - p_2} \frac{\pi r^3}{8L} \frac{pr}{\eta}; \quad \dots \quad (1)$$

(Poiseuille—viscous flow at ordinary pressures.)

$$T = \frac{Q}{p_1 - p_2} = \frac{4\sqrt{2\pi}}{3\sqrt{\rho}} \frac{r^3}{L} \cdot \dots \quad (2)$$

(Knudsen—molecular flow at low pressures.)

Knudsen \* has suggested that for intermediate pressures the formulæ can be combined in the following way :

$$\frac{Q}{p_1 - p_2} = \frac{\pi r^3}{8L} \frac{pr}{\eta} + \frac{4\sqrt{2\pi}}{3\sqrt{\rho}} \frac{r^3}{L} \cdot \frac{1 + 2\sqrt{\rho} \cdot pr\eta^{-1}}{1 + 2 \cdot 47 \sqrt{\rho} \cdot pr\eta^{-1}} \quad (3)$$

Another, more empirical, expression has been given by Todd † in terms of a variable coefficient of velocity  $\eta_p$  :

$$\eta_p = \eta(1 - e^{-kpr}). \quad \dots \quad (4)$$

We find, by revising Todd's results, that they can equally well be represented by the formula

$$\eta_p = \eta \cdot \frac{pr}{pr + k}, \quad \dots \quad (5)$$

and this can be put into a form which is similar to Knudsen's, and is generally more useful,

$$T = \frac{Q}{p_1 - p_2} = \frac{\pi r^3}{8L} \frac{pr}{\eta} + K \cdot \frac{r^3}{L} \cdot \dots \quad (6)$$

This form is to be preferred, because no physical meaning can be given to the term viscosity when intramolecular collisions are negligible compared with boundary collisions.

\* Knudsen, *Ann. d. Phys.* xxviii. p. 75 (1909).

† Todd, *Proc. Durham Phil. Soc.* vi. p. 8 (1920).

It is unfortunate that this formula cannot also be tested by Knudsen's more extensive set of results; but Knudsen does not record the values of  $p_1$  and  $p_2$  separately. An important difference between the expressions (3) and (6) is that the former indicates the existence of a minimum value of  $T$  at a certain pressure. We have calculated the  $T, p$  curves from Todd's results, and, though they show less consistency than Knudsen's, it is clear that for five different tubes, and through a complete range of pressures, there is no sign of this minimum. It may be noted that the experiments of Timiriazeff\*, by a rotating cylinder method, show no minimum in the variation of a similar function.

Both expressions are only strictly applicable (without detailed integration along the tube) when  $p_1 - p_2$  is very small, unless the  $T, p$  curve shows little curvature. For if the curvature is considerable, the apparent mean point for two widely different pressures must differ very much from the actual mean point deduced from the graph. The experimental results here recorded support the view that there is no great curvature and probably no minimum in this graph; and they support very clearly the general assumption that  $Q$  depends only upon  $p_1 - p_2$  and  $p_1 + p_2$ , and not upon  $p_1$  and  $p_2$  separately.

#### IV.

A preliminary analysis may be made of the state of the gas when a discharge is passing. Molecules, atoms, ions, and electrons are all present. The tube is filled with a sensibly uniform positive column, in which the electric force is uniform, and, according to J. J. Thomson's experiments by the positive ray analysis method, there are no negative ions present. There is no evidence of a high temperature in the gas, and the molecular dissociation, like the ionization and excitation of both atoms and molecules, is mainly due to electronic collisions, and very little to intramolecular ones. The influence of this dissociation on the viscosity, at the higher pressures, may be roughly estimated in the following way.

Let the diameters and masses of the molecules and atoms be  $d_m$ ,  $m$ , and  $d_a$ ,  $\frac{1}{2}m$  respectively. The viscosities of the molecules and atoms separately may be given by

$$\eta_m = \frac{mv_m}{2.88\pi d_m^2}, \quad \eta_a = \frac{\frac{1}{2}mv_a}{2.88\pi d_a^2}.$$

\* Timiriazeff, *Ann. d. Phys.* xl. p. 971 (1913).

We may write

$$\frac{1}{2}mv_m^2 = \frac{1}{2} \cdot \frac{1}{2}m \cdot v_a^2;$$

and for the relation between the two diameters we note that Rankine's \* calculation for a molecule made up of two rare gas atoms gave

$$d_a^2 = 0.61dm^2,$$

and we assume the same relation here. The result is then

$$\eta_m = 0.86\eta a.$$

If we suppose that one-half of the molecules are dissociated—a very large over-estimate,—the viscosity of the mixture can be calculated by one of the two usual expressions for gas mixtures, and we have taken that due to Pulu†. We neglect the tendency of two atoms to re-unite, and also the forces which divide them again. The result so found is

$$\eta = 1.10\eta_m,$$

so that this large amount of dissociation produces a slight increase in viscosity. There is a small rise in temperature which acts in the same direction, and there is an increased force of repulsion between such atoms as are positively charged, also tending to increase the viscosity.

In the Bohr model of the atom the excited and luminous atom is distinguished by an outer electron or electrons circulating in a very much enlarged orbit, and the atom may therefore be increased in area very greatly. This would lead to a large decrease in viscosity, were it not that the orbits in this model are plane ones and the change in the mean collision area presented by the molecule is less than the change in the area enclosed by the orbit. Moreover, the number of atoms affected at any instant, both as to excitation and to ionization, is a very small fraction of the total number present. If the pressure is 1 mm., and a current of 10 milliamperes passes through the capillary tube, mostly carried by electrons, then a simple calculation shows that for every molecule in the tube about 100 electrons pass through the tube in every second. If the excitation time for the molecule is of the order of  $10^{-8}$  second, then very few will be in that enlarged state at any instant.

The direction of the discharge through the flowing gas

\* Rankine, *Proc. Roy. Soc.* xcvi. p. 360 (1921).

† Pulu, *Wien. Ber.* lxxix. p. 112 (1879); see also Thomson, *Ann. d. Phys.* xxxvi. p. 815 (1911), and Gille, *Ann. d. Phys.* xlviii. p. 799 (1915).

must also influence the flow, for it governs the motion of the electrons, and we have not yet considered the electron molecule collisions. The mean velocity of the electrons in the discharge tube has been examined by Compton \*, and on the basis of his theory we find that the total contribution of their momentum to the movement of the molecules is less than could be observed in our experiments. The experimental results actually show no change in the rate of flow when the current is reversed. J. J. Thomson † has indicated one further cause of pressure variations within a discharge tube—the flow of positive ions; but this effect is confined to the dark space, and is not measured by the present apparatus.

In the case of the lowest pressures, the molecular flow of atoms and of molecules may proceed independently. Suppose that the inflow pressure,  $p$ , is made up of  $p_{1a}$  due to atoms and  $p_{1m}$  due to molecules, and similarly with  $p_2$ . Then, according to Knudsen's method (Knudsen did not consider mixtures), the quantities flowing through the capillary are

$$Q_a = \frac{k}{\sqrt{\rho_a}} (p_{1a} - p_{2a})$$

and

$$Q_m = \frac{k}{\sqrt{\rho_m}} (p_{1m} - p_{2m}),$$

where  $k$  depends only on the dimensions of the tube. The total quantity is given by

$$Q = Q_a + Q_m = k \left\{ \frac{p_{1a} - p_{2a}}{\sqrt{\rho_a}} + \frac{p_{1m} - p_{2m}}{\sqrt{\rho_m}} \right\}.$$

Making the same assumptions as in the previous case of viscous flow, we now write

$$\rho_m = 2\rho_a \quad \text{and} \quad p_a = 2p_m = \frac{2}{3}p_1,$$

and the formula becomes

$$Q = 1.28 \frac{k}{\sqrt{\rho_m}} (p_1 - p_2),$$

The effect of ionization is therefore to *increase*  $Q$ , and this is analogous to a decrease of viscosity. In this case, then, the effects of ionization and excitation are in the same direction, and we might expect a small measurable change at the lowest pressures for large currents.

\* Compton, Phys. Rev. xxii. p. 333 (1923), and xxiv. p. 507 (1924).

† Thomson, Phil. Mag. xlviii. p. 1 (1924).

*Summary.*

1. Measurements have been made of the molecular and viscous flow of gases in fine capillary tubes at low pressures.

2. The rate of flow is found to be unaffected, to within less than 5 per cent., by an electric discharge passing through the flowing gas. A theoretical discussion suggests that an effect is to be expected with diatomic gases at very low pressures.

3. Observations have been made of the disappearance and emission of gas in discharge tubes. The change of pressure follows an exponential law when it occurs, and under special circumstances there may be no change.

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XXXIX. *The Optical Anisotropy of some simple Inorganic Gaseous Compounds.* By K. R. RAMANATHAN, M.A., D.Sc., and N. G. SRINIVASAN, B.Sc., Physics Department, University College, Rangoon\*.

*Introduction.*

FROM the time that Lord Rayleigh discovered the imperfection of polarization of the transversely scattered light in gases, it has been the hope of physicists that some time or other it would lead to important knowledge regarding the structure of atoms and molecules. In his recent work on the doubly refracting properties of typical inorganic crystals, W. L. Bragg† has made use of the idea of the mutual influence of the polarization of the different atoms of the crystals, and has deduced results which are in general agreement with observation. In this work, Bragg assumes with Wasastjerna that the atoms are in an ionized condition: that is, they have given up or taken in a sufficient number of electrons so that the electronic structure of each ion approaches closely that of the nearest inert gas. He further assumes that each ion by itself can be considered optically isotropic.

One of the authors has recently shown that the optical anisotropy of some of the common inorganic gases‡ which is evidenced by the imperfection of polarization of the transversely scattered light in these gases, can be likewise explained if we take into account the mutual influence of the

\* Communicated by the Authors.

† Proc. Roy. Soc. A, vol. cv. p. 370 (1924).

‡ Proc. Roy. Soc. A, vol. cvii. p. 684 (1925).



polarizations of the different atoms in the molecule. The work has later been extended to the organic molecules benzene and cyclohexane, but in all the cases that have been hitherto examined the gases are of the "homo-polar" or shared-electron type.

With a view to getting some idea of the optical anisotropy of the "hetero-polar" molecules, experiments have been made on a few simple hydrides. The inert gases are known to possess a high degree of symmetry, and the experiments of Lord Rayleigh \* on argon and of Capannes and Lépape on xenon and krypton † show that the optical anisotropies of these molecules are very small, the values of the imperfection of polarization of the transversely scattered light in these gases being respectively .0046, .0055, and .0055. Hydrides of elements adjoining the inert gases, like those of the halogens, would, it is believed, assume electronic structures similar to those of the inert gases, with perhaps a slight deformation of the symmetrical structure caused by the presence of the hydrogen nuclei. The gases  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  may be expected to approach neon, while  $\text{SiH}_4$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$  would approach argon.

In the following paper the results obtained with ammonia, sulphuretted hydrogen, and hydrochloric acid are described and discussed.

### *Experimental.*

The apparatus employed was of the usual type, being a rectangular metal cross-tube of 5 cm. internal diameter. Each arm of the cross was 27 cm. in length. The tube was coated inside with black enamel which on heating gave a hard glassy coating. Three ends of the cross were closed with plane glass plates sealed on with sealing-wax or hard paraffin, while the fourth end was closed with a metal cap. An oblique metal plate with a uniform glassy coating of black enamel was placed near the closed end so as to reflect away any stray light which might reach that end. Suitable blackened metallic apertures were placed in the different arms so as to shut out stray light. The cross was also provided with two side tubes, one to serve as an inlet for the gas and the other to serve as an exit.

After drying and cleaning, the apparatus was exhausted by means of a pump and the dry dust-free gas was slowly let in. During the experiment a continuous stream of the

\* Proc. Roy. Soc. A, vol. xciii. p. 57 (1920).

† Comptes Rendus, clxxix. p. 325 (1924).

gas was kept running. The measurements of depolarization were made in the usual manner by means of a Wollaston double-image prism of quartz and square-ended nicol with a small low-power reading telescope placed behind the nicol.

The pure gases were prepared in the following manner:—

(a) *Hydrochloric acid gas.*

By the action of strong sulphuric acid on sodium chloride. The gas was dried by passing over fresh phosphorus pentoxide.

(b) *Hydrogen sulphide.*

By heating antimony trisulphide with concentrated hydrochloric acid. It was found that free evolution of gas was helped by mixing the antimony sulphide with clean sand. The gas was first bubbled through water to remove the acid spray and then dried over phosphorus pentoxide.

(c) *Ammonia.*

By warming a concentrated solution of ammonia. The gas was passed through a lime tower to remove moisture.

Usually for observations on the scattering of light in gases, the dust particles that are invariably present are removed by slow passage through a tube packed with cotton-wool. As it was, however, found that cotton-wool was slowly attacked by HCl, it was replaced throughout the experiments by clean dry asbestos wool, which was found to be a good substitute.

*Error due to convergence of the Incident Rays.*

Before discussing the experimental results, it is worth while to consider a source of error which, while unimportant when measuring the imperfection of strongly depolarizing substances, becomes of considerable importance when small values of depolarization are measured\*. When the incident beam is focussed by means of a lens, and the imperfection of polarization is measured in a direction perpendicular to the average direction of the beam, the value obtained would be different from what it would be if the beam were strictly parallel. The error would be greater the greater the convergence of the beam. To find its amount, consider a beam of plane polarized light with its electric vector parallel to OZ moving along the X-axis. When observed along OY, let the Z-component of the intensity of the scattered light be A and the X-component B; then, when the incident light

\* Lord Rayleigh, Proc. Roy. Soc. A, vol. xcv. p. 161.

is unpolarized, the components will be  $A + B$  and  $2B$  respectively. If the direction of observation be changed by an angle  $\theta$ , the principal components in a plane perpendicular to the scattered ray will become  $A + B$  and  $B(1 + \cos^2 \theta) + A \sin^2 \theta$  respectively, and thus the observed ratio of the weak component to the strong will be

$$\rho_{\theta} = \frac{A \sin^2 \theta + B(1 + \cos^2 \theta)}{A + B} = \frac{2B + (A - B) \sin^2 \theta}{A + B},$$

which differs from  $\rho$ , the value in a transverse direction, by  $(A - B) \sin^2 \theta / (A + B)$ .

In our present case,  $\sin \theta$  varies from  $-a/d$  to  $a/d$  where  $2a$  is the aperture of the lens, and  $d$  is the distance from the lens at which the rays are focussed\*.

We have, therefore, to find the average values of  $\rho_{\theta}$  when  $\theta$  varies through this range. A simple integration and averaging give for the ratio of the weak component to the strong in a direction perpendicular to the average direction of the beam

$$\frac{H}{V} = \frac{2B + (A - B) \sin^2 \theta / 2}{A + B}.$$

In the case of a gas producing an imperfection of polarization of 0.01 in a strictly perpendicular direction, the error caused by the non-parallelism of the incident rays will be as much as 0.038 when  $\theta$  is  $5^\circ$  and 0.014 when  $\theta$  is  $3^\circ$ .

Similar errors will be caused by a wrong adjustment of the double-image prism and by the direction of observation not being exactly perpendicular to the incident beam. The former error can be avoided by a careful adjustment of the double-image prism; the latter is usually small in visual observations, but it is one to be borne in mind when measurements are made photographically where the temptation is to use a large aperture in order to secure economy of light.

### *Results.*

The observed value of the ratio of the weak component to the strong in the transversely scattered light in each of the gases  $\text{HCl}$ ,  $\text{H}_2\text{S}$ , and  $\text{NH}_3$  was found to be the same, namely 0.010. The measurements were repeated on different days, and consistent results were obtained. There was no evidence of fog formation in any of the cases. In changing from one gas to another the whole apparatus was overhauled and

\* With the small angles usually employed, the distinction between  $\sin \theta$  and  $\tan \theta$  may be dropped.

thoroughly cleaned, and the inside of the tube was repainted. The maximum angular divergence of the rays from the axis was measured to be  $3^{\circ}8$ , and hence the error due to the non-parallelism of the incident rays was  $\cdot002$ . If we subtract this from the value obtained above, we get for all the three gases the corrected value  $\cdot008$ .

It is remarkable that the values of  $\rho$  for all these gases should be so low, and that they should all be equal to each other. They are also of the same order of quantities as the values obtained for the inert gases. As mentioned above, Lord Rayleigh obtained the value  $\cdot0046$  for argon, which, however, has not been corrected for the non-parallelism of the incident rays. Lord Rayleigh estimated the extreme divergence of the incident rays from the axis to lie between  $3^{\circ}$  and  $4^{\circ}$ , and the angle subtended by the aperture of the camera was of the same order. The corrected value would be only about  $\cdot0025$ . Whether this residual effect does exist or not is worth re-examination.

It is now generally believed that in hydrochloric acid gas the electron belonging to the hydrogen atom has gone over to the chlorine atom to form one of its outermost orbits, thus completing the argon configuration, and similarly in sulphuretted hydrogen the two electrons from the hydrogen atoms have been transferred to the outermost orbits of sulphur. The smallness of depolarization of these gases supports this view. Likewise in ammonia, the additional electrons belonging to the three hydrogen atoms may be looked upon as having been transferred to the nitrogen to complete the neon configuration. Although no measurement of the depolarization of the transversely scattered light in neon are available, it may be expected to be small.

The cases of carbon monoxide and nitrogen are interesting. Langmuir and others have suggested that the configurations of the outer electrons of these gases are similar. If that is so, we expect that the optical anisotropies of the two gases should be nearly the same. Visual measurements made with sunlight at Calcutta show that carbon monoxide shows a depolarization of 3.4 per cent., while for nitrogen Lord Rayleigh\* obtained the value 4.06 per cent. by the photographic method. On the other hand, if we calculate the depolarization of nitrogen from the visual measurements of Raman and Rao† on air (4.37) and oxygen (8.4), we obtain the value 3.5 per cent. For purposes of comparison

\* Proc. Roy. Soc. A, vol. xcvi. p. 435 (1920).

† Phil. Mag. vol. xlv. p. 427 (1923).

it is better to choose the values obtained by the same method, and the closeness of the values obtained by the visual method is very striking.

*Summary.*

In the foregoing paper, measurements of the depolarization of the light scattered by the gases hydrogen chloride, sulphuretted hydrogen, and ammonia are described, and the results obtained are discussed in their relation to the structure of the molecules. The depolarization in a direction perpendicular to the incident beam was in all cases the same, namely .008, indicating a high degree of optical symmetry. The value of the anisotropy supports the view that in these gases the electrons belonging to the hydrogens have gone over to the outer orbits of the heavier atoms, in order to complete the electronic structure characteristic of the nearest inert gas. It is also pointed out that the values of the depolarization of nitrogen and carbon monoxide, both obtained visually, have practically the same value, supporting the view that the configurations of the outer electrons of these molecules are similar. The error caused in the measurement of the depolarization of the light scattered by substances owing to the non-parallelism of the incident light is discussed.

**XL. *Some Considerations of the Reaction Constant Equation, and a Simple Method of determining the End Point.***  
By ROBERT CHRISTIE SMITH, *Carnegie Teaching Fellow, University of Glasgow* \*.

**I**N the determination of the velocity constant for a monomolecular reaction use is made of the equation

$$k = \frac{1}{t} \log \frac{a}{a-x}.$$

For a practical solution of this equation it is necessary to determine the concentrations "*a*" and "*x*," or at least numbers proportional to them. This is usually done by a series of measurements (titrations, polarimetric readings, etc.) commencing with the first taken immediately on mixing the reactants and ending with the final reading taken on completion of the reaction. To obtain the final reading it is necessary either to weigh a sample of known purity (*e. g.* of the ester, in a hydrolysis with acid) or wait at least 48 hours till the reaction is completed. It is, however,

\* Communicated by the Author.

possible to obtain simply the required end point from the following considerations.

If  $\tau_0, \tau_1, \tau_2, \dots, \tau_r, \dots, \tau_\infty$  denote the readings obtained in the usual manner, it is possible to construct the following series from it.

$$\begin{aligned}\tau_1 - \tau_0 &= T_1, & \tau_n - \tau_0 &= T_n, \\ \tau_2 - \tau_0 &= T_2, & \tau_\infty - \tau_0 &= T_\infty,\end{aligned}$$

when the equation for a monomolecular reaction becomes

$$k = \frac{1}{t} \log \frac{T_\infty}{T_\infty - T_n},$$

$$\text{i. e.} \quad (e^k)^t = \frac{T_\infty}{T_\infty - T_n} \quad \text{or} \quad (e^{-k})^t = 1 - \frac{T_n}{T_\infty};$$

$$\text{hence} \quad (e^{-k})^{t_n} = \left(1 - \frac{T_n}{T_\infty}\right)^{t_n} = \left(1 - \frac{T_{n+1}}{T_\infty}\right)^{t_{n+1}} = \dots$$

If  $t_{n+1} = 2t_n$ , then

$$\left(1 - \frac{T_n}{T_\infty}\right)^2 = \left(1 - \frac{T_{n+1}}{T_\infty}\right),$$

or solving

$$T_\infty = \frac{T_n^2}{2T_n - T_{n+1}}.$$

Hence it is possible by calculation to obtain the "end point" from two values obtained at specified times such that the one time is half the other. It is to be noted that while the probability is that if a constant value is obtained for  $T_\infty$  then the reaction is monomolecular, but this cannot be strictly proved mathematically.

It is not possible for accurate results to be obtained by readings taken immediately the reaction starts, as at this point, besides the readings being as a rule slightly irregular, the value  $(2T_n - T_{n+1})$  is small and any absolute error therein is magnified in the determined end point. This is most easily demonstrated if the constant and end point are assumed and the values  $T_n$  and  $T_{n+1}$  are calculated.

$$\text{E. g., let} \quad k = 0.0023 \quad \text{and} \quad T_\infty = 20,$$

$$\text{then} \quad T_n \log \frac{20}{20 - T_n} = 0.01 \quad \text{for} \quad t = 10,$$

$$T_{n+1} \log \frac{20}{20 - T_{n+1}} = 0.02 \quad \text{for} \quad t = 20.$$

With four-figure logarithms  $2T_n - T_{n+1} = 0.110$ .

With eight-figure logarithms  $\phantom{2T_n - T_{n+1}} = 0.0051813$ .

*Phil. Mag.* S. 7. Vol. 1. No. 2. Feb. 1926. 2 K

However, as time goes on the value calculated by four-figure logarithms (which usually covers the accuracy of the titration etc.) becomes constant and dependable, as seen from the results in Table II. A theoretical set of results are given in Table I.

TABLE I.

Test equation.—Constant =  $\cdot 015$ . End point = 20.

Value of $s$ at			4 fig. logs.
10 mins.	=2.7866333		
		=19.94623	19.96
20 "	=5.1849537		
		=20.00102	20.00
40 "	=9.025789		
		=19.99996	20.00
80 "	=13.978334		
		=19.99992	20.01
160 "	=18.186976		

TABLE II.

Actual results.

End point.	
Calculated.	Found.
3.48	3.47
3.64	3.61
8.58	8.59

TABLE III.

Effect of error in end point value on  $K$ .

End point value =21.		=19.
$K = \cdot 01426$	at 10 mins.	$\cdot 01585$
$\cdot 01416$	20 "	$\cdot 01593$
$\cdot 01406$	40 "	$\cdot 01613$
$\cdot 01370$	80 "	$\cdot 01664$
$\cdot 01257$	160 "	$\cdot 01972$
Correct value = 20 as in Table I.		

The method can be extended to bimolecular etc. reactions, but the expression for  $T_{\infty}$  becomes more complicated.

Again considering the equation,

$$k = \frac{1}{t} \log \frac{T_{\infty}}{T_{\infty} - T_n}.$$

If there is an error " $\alpha$ " in the end point it becomes

$$k = \frac{1}{t} \log \frac{T_{\infty} + \alpha}{T_{\infty} + \alpha - T_n}.$$

As this fraction  $\left(\frac{T_{\infty}}{T_{\infty} - T_n}\right)$  is always greater than 1, the addition of an equal amount to the numerator and denominator will decrease its value, and as it becomes greater the decrease will become greater, and similarly if the error is negative its value will be increased. Hence in the first case, instead of a constant  $k$ , a series of decreasing values, and in the second a series of increasing values will be obtained. If, therefore, the reaction is known to be monomolecular the final reading  $T_{\infty}$  can be obtained by a method of trial and error. The effect can also be shown graphically by plotting " $t$ " against  $\left(\log \frac{T_{\infty}}{T_{\infty} - T_n}\right)$ .

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## XLI. The so-called Positive Photo-Electric Emission (Inverse Effect), and the Reality of the Sub-Electron. By EDWARD J. LORENZ \*.

### I. Introduction.

A FEW observers have reported the discharge of positive electricity produced by ultra-violet light. Dember† found that a metal plate exposed to ultra-violet light *in vacuo* had the power to communicate a positive charge to a receiving cylinder when the proper accelerating field was applied. His experiments have recently been repeated by Du Bridge‡, who reports that Dember's results can be entirely accounted for on the basis of the photo-electric effect produced on the collecting cylinder by scattered ultra-violet light against which no precautions had been taken.

\* Communicated by Prof. R. A. Millikan.

† Dember, *Ann. der Phys.* iii. p. 137 (1909).

‡ Du Bridge, *Phys. Rev.* p. 201 (Feb. 1925).



His conclusions are: "there is no measurable photo-electric production of either gaseous or metallic positive ions by the range of wave-lengths emitted by the quartz mercury lamp."

R. Bär and F. Luchsinger\*, working with small particles of paraffin and selenium in a Millikan electron apparatus, found that some of the particles showed the inverse effect—that is, they became charged negatively when illuminated by ultra-violet light. This has been construed by some workers as indicating the discharge of positive electricity. However, as they were only using the ultra-violet light to charge up their particles in order to measure the charge communicated, and were not interested in the source of the photo-electrons, it is natural to assume that no special precautions were taken against the light striking the metallic plates of the condenser. The photo-electrons liberated from these metal surfaces being caught by the paraffin and selenium particles would make it seem as if the particles had lost a positive charge. S. Taubes†, working in the same laboratory as Luchsinger and Bär and presumably with the same apparatus, reported this inverse effect when dealing with particles that had a large positive charge, and showed that it is due to the photo-electrons given off by the condenser plates, for when these were coated with paraffin the inverse effect entirely disappeared.

M. Hake‡, working at Vienna and using a diminutive Millikan electron apparatus designed by Prof. Ehrenhaft, has recently reported results on nineteen different materials. He found that metals show both the inverse and the normal effect, depending on the gas in which the metal particles are suspended, and that some insulators, for example glycerine, always show the inverse effect in all gases. Wasser§, working in the same laboratory as Hake, gives results on mercury drops in N and CO<sub>2</sub>. He claims that drops of larger radius than  $1.9 \times 10^{-5}$  always show the normal effect, that those between  $1.1$  and  $1.9 \times 10^{-5}$  cm. show both the normal and the inverse effect, while those of smaller radius than  $1.1 \times 10^{-5}$  cm. always show the inverse effect.

The following investigation was undertaken to test the correctness of the foregoing conclusions, and to determine whether the changes in charge experienced by minute mercury droplets are of a magnitude corresponding to the

\* F. Luchsinger, *Ar. Sc. Phys. et nat.* i. p. 544 (1919); R. Bär and F. Luchsinger, *Phys. Zeit.* xxii. p. 227 (1921).

† S. Taubes, *Ann der Phys.* vi. p. 646 (1925).

‡ M. Hake, *Zeit. f. Phys.* Bd. xv. Heft 2-3 (1923).

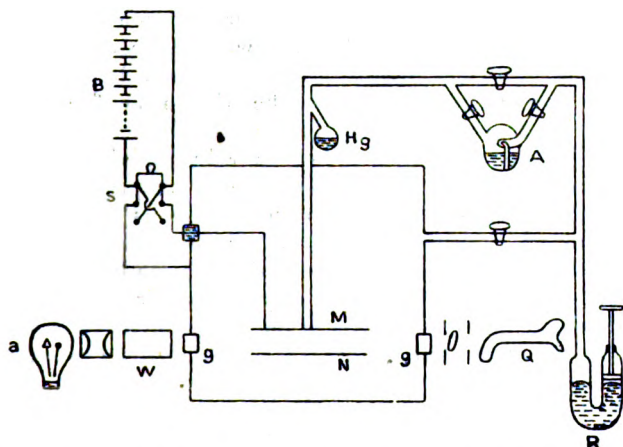
§ E. Wasser, *Zeit. f. Phys.* Band xxvii. Heft 4 (1924).

electronic charge or to a charge smaller than this, as the Vienna physicists have maintained\*.

## II. Method.

The apparatus used in the work consisted of a Millikan condenser such as has been used by Millikan and his pupils during the past fifteen years. Fig. 8, p. 118 of 'The Electron'†, by Millikan, shows a cross-section. Fig. 1 shows a diagrammatic scheme of the apparatus. The illumination was pushed to its limit. The light which entered the window "g" was produced by a 500 c. p. point-light, the rays of which were concentrated by a

Fig. 1.



powerful condensing lens. At 90° to this window was a quartz window through which a beam of ultra-violet light which had been concentrated by a quartz lens and passed through the proper diaphragms so as to avoid striking the plates M and N, was allowed to pass. This ultra-violet light could be turned on and off by raising or lowering a shutter operated by a foot pedal.

The gases used were washed and filtered by slowly bubbling them through water, then through concentrated H<sub>2</sub>SO<sub>4</sub>, and finally passing them through a long tube filled with CaCl<sub>2</sub>. The ends of the tube were plugged with glass wool. The nitrogen was also washed in a tower containing copper shavings over which a solution of NH<sub>4</sub>OH and

\* Phil. Mag. vol. xlix. (April 1925).

† Rev. Ed., University of Chicago Press, 1924.

$\text{NH}_4\text{Cl}$  continuously passed. It was also bubbled through a bottle of strong  $\text{KOH}$  so as to remove any  $\text{CO}_2$ . Only three cubic centimetres per second passed; this gave the cleansing agents ample time to act.

In making observations the substance under test was blown over from the atomizer A by means of a mercury compressing device R which allowed the gas to be taken from the test chamber and returned through the atomizer without any danger of being contaminated. In the case of mercury the drops were produced by substituting the mercury boiler Hg for the atomizer A. When the drops, whatever their nature, were observed through the telescope and the battery then connected, the charged particles were at once swept out of the field, only the neutral ones being left. With the field still on, the ultra-violet light was then directed upon the drops, and the speeds observed with the battery first connected one way, then the other. In order to test whether or not the rays from the quartz lamp had the power of ionizing the gas, drops that were normally very sensitive were charged and held suspended in the field of view by applying the proper potential difference. A narrow strip of opaque material was then placed across the quartz window so as to protect the drop from the direct influence of the ultra-violet light, but to allow the gas on either side of the drop to be illuminated. With this arrangement, prolonged exposure to the ultra-violet light, for ten minutes or more, produced no change in the charge of the drop, thus proving that the gas around it was not affected by the ultra-violet light.

### III. Qualitative Results.

Fifty drops of oil varying in apparent radius from  $1.6$  to  $3 \times 10^{-5}$  cm. were observed in air,  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{He}$ . In no case was any effect observed. When the screens that kept the ultra-violet light off the plates were removed, the inverse effect was immediately detected.

Fifty drops of glycerine of about the same range of diameters were observed in air,  $\text{N}_2$ , and  $\text{H}_2$ . In no case was it possible to detect any effect. The removal of the screens shielding the plates again produced the inverse effect.

A long series of experiments was conducted with Hg drops in air and in  $\text{N}_2$ . Fifty different drops of mercury, varying in apparent radius from  $1.4$  to  $8.4 \times 10^{-5}$  cm., were illuminated with ultra-violet light more than 80 different times when neutral and when charged with various charges, sometimes positive, sometimes negative. In no case was an increase of the negative or a decrease of the positive charge observed.

Whenever a change occurred it was always of the normal type. The radii of these drops were computed by Millikan's\* method. When Wasser's method is used they correspond to a range from  $\cdot 95$  to  $8.4 \times 10^{-5}$  cm. Both methods use the assumption (shown below to be incorrect) that the density of all the particles is 13.6. They differ only in that Wasser's computations depend upon the assumption of a somewhat incorrect law of fall, while Millikan's method avoids this source of error. Wasser's range was from  $\cdot 7$  to  $3.3 \times 10^{-5}$  cm. I have, therefore, worked over practically the same range of droplet-radii as did he.

Another method, and one which is, I think, an improvement upon the foregoing procedure, used by Wasser, was to charge the drops slightly by  $\gamma$ -rays and then adjust the applied potential so as to just balance the drop. In this way a single drop could be floated in the field of view for 30 minutes or an hour at a time, and thus the exposure time to the ultra-violet light increased. *In no case was an inverse effect noted.* Under this prolonged exposure to the ultra-violet light, drops that were ordinarily classified as insensitive sometimes charged up in the normal way. *When the screens that shielded the plates from the ultra-violet light were removed, the drops showed the inverse effect after a very short exposure.*

Our conclusions are that the inverse effect, reported by Hake and Wasser as indicating a discharge of positive electricity, has no real existence. It is a spurious effect produced by stray or scattered ultra-violet light striking the plates of the condenser and liberating photo-electrons, which are caught by the drop in the apparatus. The correctness of this conclusion is suggested by the dimensions of Hake and Wasser's condenser, namely  $9 \times 9 \times 2$  millimetres. In such a condenser it is clearly extraordinarily difficult, if not altogether impossible, to make a concentrated beam of ultra-violet light pass through the 2-millimetre opening without its striking somewhere and scattering over the entire area of the plates. Our apparatus had the plates 15.3 mm. apart, and was therefore better suited for testing the effect of letting the light strike the drop alone, the plates alone, or both together.

#### IV. Reality of the Sub-Electron.

In the same region of radii in which Wasser finds that mercury droplets show the inverse photo-electric effect, he also finds that the charge or change of charge on the droplets

\* Millikan, 'The Electron,' p. 104.

is far below the accepted value of the electron—that is, below  $4.77 \times 10^{-10}$  E.S.U.

In order to test whether or not changes of charge of smaller value than the electron are indeed ever produced by ultra-violet light, or otherwise, in drops of any size or kind, a long series of experiments was carried out. My results are in agreement with Wasser's in that the apparent charges obtained on some of the drops, using Wasser's method of computing, fall below  $4.77 \times 10^{-10}$  E.S.U. *But, the real test of the existence of the sub-electron in this experiment consists in finding whether all the charges obtainable on a given drop are exact multiples of the smallest charge which it is ever found to carry.* Millikan\* has emphasized this in one of his recent papers.

The justification for the foregoing statement is that Millikan and many other workers have shown that the smallest charge caught on an oil drop or any other kind of particle *when ionization is produced in the surrounding gas* is always  $4.77 \times 10^{-10}$  E.S.U., or some multiple of this unit irrespective of the size of the drop. If, then, when we are dealing with a mercury droplet we find that the charge given to it by an electron caught *from the surrounding gas*, which has been ionized by  $\gamma$ - or X-rays, is exactly the same as the charge given to it by being illuminated by ultra-violet light, it follows that the latter charge has also the value  $4.77 \times 10^{-10}$  E.S.U. Any contrary results obtained on the basis of an assumed density must perforce be ascribed to a wrong assumption as to this drop-density.

In the accompanying Tables I., II., and III. the column headed  $\frac{v_1 + v_2}{n}$  shows how perfectly the multiple relationship holds with precisely the same sort of drops used by Wasser, and obtained under precisely the same conditions that he used when he thought he got sub-electrons by the photo-electric process. Table I. shows results on a droplet that was very sensitive to ultra-violet light. Table II. shows results on a drop that showed only slight sensitivity. The results in Table III. were obtained with a drop that was not affected by the ultra-violet light, even after several minutes exposure. These three tables are typical of results that were obtained on at least twenty-five different drops that were tested for multiple relationship, about half of them in air and half in pure nitrogen. Some of these drops were carried through twenty changes of charge. In no case was the

\* Millikan, Phys. Rev. p. 101 (July 1925).

variation of  $\frac{v_1 + v_2}{n}$  more than 1.5 per cent. from the mean, even though the readings were taken merely with a stop-watch, and therefore not with very great precision.

TABLE I.  
Sensitive drop.  $p$  74 cm.

Change in charge produced by	Stop-watch Readings.		Average. $v_1$ .	$v_2$ .	$v_1 + v_2$ .	$n$ .	$\frac{v_1 + v_2}{n}$ .
	$T_g$ .	$T_f$ .					
	47.0	24.5	0.1120	0.2171	0.3291	-1	0.329
U. V. L. ....		24.2	"	0.2194	0.3314	+1	0.331
Spontaneous .....	47.1	9.4	"	0.5553	0.6673	+2	0.334
Spontaneous .....	47.4	23.9	"	0.2226	0.3346	+1	0.335
U. V. L. ....		9.4	"	0.5553	0.6673	+2	0.334
U. V. L. ....		4.3	"	0.12372	0.13492	+4	0.337
	48.3						
Volts.....				1925	$a$	$2.3 \times 10^{-5}$	
Distance between cross hairs...				532 cm.	$e_1$	$7 \times 10^{-10}$	
Distance between plates.....				1.53 cm.			

TABLE II.  
Slightly sensitive drop.  $p$  74.1 cm.

Change in charge produced by	Stop-watch Readings.		Average. $v_1$ .	$v_2$ .	$v_1 + v_2$ .	$n$ .	$\frac{v_1 + v_2}{n}$ .
	$T_g$ .	$T_f$ .					
	63.2	4.2	0.0841	0.12666	0.1507	-13	0.104
Spontaneous .....		9.7	"	0.5484	0.6325	-6	0.105
U. V. L. ....		12.1	"	0.4396	0.5237	-5	0.105
Spontaneous .....	64.0	15.9	"	0.3325	0.4166	-4	0.104
U. V. L. ....		42.0	"	0.1266	0.2107	-2	0.105
Spontaneous .....	61.6	242.0	"	0.0219	0.1060	-1	0.105
Volts.....				900	$a$	$2.4 \times 10^{-5}$	
Distance between cross hairs...				532 cm.	$e_1$	$4.2 \times 10^{-10}$	
Distance between plates.....				1.53 cm.			

TABLE III.

Insensitive drop.  $p$  74 cm.

Change in charge produced by	Stop-watch Readings.		Average. $v_1$ .	$v_2$ .	$v_1 + v_2$ .	$n$ .	$\frac{v_1 + v_2}{n}$ .
	$T_g$ .	$T_f$ .					
		3.4	0.0232	.15647	.15879	+6	.0264
Spontaneous .....	228.8	10.6	„	.05001	.05233	+2	.0262
Spontaneous .....	228.4	6.8	„	.07823	.08056	+3	.0268
Radium.....		21.9	„	.02429	.02661	+1	.0266
Radium ... ..		21.9	„	.02429	.02661	-1	.0266
Spontaneous .....	228.6	10.6	„	.05001	.05233	-2	.0262

Volts.....	1925	$a$	$1.5 \times 10^{-5}$
Distance between cross hairs...	.532 cm.	$e_1$	$2.6 \times 10^{-10}$
Distance between plates .....	1.53 cm.		

Here, then, we have the proof that the smallest quantity of electricity that any drop takes on is  $4.77 \times 10^{-10}$  E.S.U., and that it is independent both of the mechanism of charging and of the size of the drop. The reason for the apparent appearance of smaller charges in Wasser's and Ehrenhaft's work is shown in the following section.

#### V. Sizes and Densities of Drops.

In calculating the radius of the drop, the equation

$$a = \sqrt[3]{\frac{3Fe_n}{4\pi g(\sigma - \rho)} \frac{v_1}{v_1 + v_2}}$$

was used (Millikan, 'The Electron,' p. 104). " $e$ " was placed equal to  $4.77 \times 10^{-10}$  E.S.U., since the multiple relationship had established the fact that the charges were all unitary charges, and since Millikan's work of the past fifteen years has fully established this value for the unit of charge. The results of this paper are, however, in no way different if  $a$  is computed from an approximate correction to Stokes's law and without any use of the value of  $e^*$ . The

\* Prof. Ehrenhaft is entirely in error in asserting that Millikan's results depend in any way upon the assumption either of a multiple relationship in drop-charges or a numerical value of  $e$ . These are both direct experimental facts. See Millikan, Phys. Rev. vol. xxvi. no. 1 (July 1925).

method adopted is merely the more convenient and the more accurate. No drops were used on which sufficient data had not been obtained to establish the multiple relationship so that  $v_2$ , the velocity under a known field, could be established for a single electron on the drop. Wasser\* uses for obtaining  $a$  the corrected form of Stokes's law of fall, namely

$$\frac{4\pi a^3 \sigma g}{3} = \frac{6\pi a v_1 y}{1 + A \frac{e}{a}}.$$

He assumes, however, that  $A$  is a constant. As a matter of fact, in the region of radii in which he thinks he works,  $A$  varies from .7 to .98, as shown by Millikan†. While, however, Wasser's method and mine always agree quite closely for droplets which are actually spheres of mercury, his method yields apparent radii as much as 30 per cent. smaller than those given by my method for droplets which are not spheres of mercury. When calculated by Wasser's method our smaller drops are as small as those he uses. Either method, however, yields only the apparent size of the smaller drops, as we shall show that the density of these is very far from that of Hg.

In order to find the charge on the drops, the value of  $e_1$  was first found by means of the equation

$$e_1 = \frac{4\pi}{3} \left(\frac{9\eta}{2}\right)^{3/2} \left(\frac{1}{g(\sigma - \rho)}\right)^{1/2} \frac{(r_1 + r_2)_0 v_1^{1/2}}{F}$$

which is derived from the uncorrected form of Stokes's law. Then  $e_1^{2/3}$  was plotted against  $1/pa$  in the familiar Millikan‡ method. Fig. 2 shows the results obtained. The very sensitive, that is the larger, drops fall on, or close to, Millikan's line, as shown in the figure, and give the correct value for  $e$ . The slightly sensitive and insensitive drops—these coincide with those which fall very slowly, and hence for which  $a$  is apparently small—give low values for  $e$ , and show no regularity in respect to position on the graph. In order to bring them upon Millikan's line, it is necessary to assume for all these irregular drops densities much lower than that of mercury—in the cases of some of them a density as low as one-ninth that of mercury. These are the droplets that Wasser assumes are pure mercury, although their densities are hereby shown

\* Wasser, *Zeit. f. Phys.* Bd. xxvii. Heft 4, p. 207 (1925).

† Millikan, *Phys. Rev.* xxii. (1923).

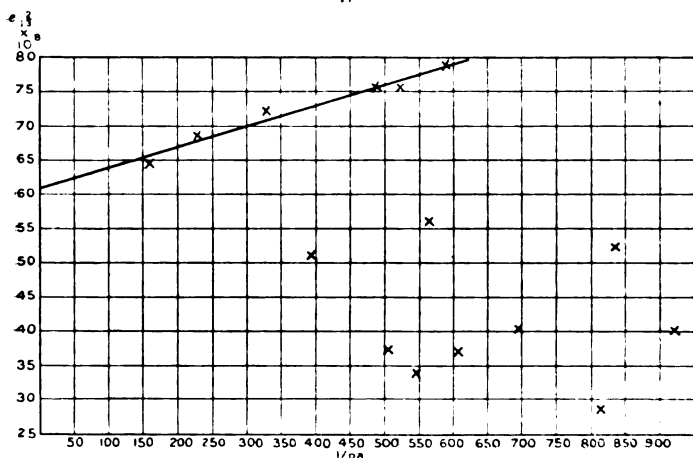
‡ Millikan, 'The Electron,' pp. 91, 105.



to be as low as 1.5. Evidently he is working with an airy cluster of some kind.

This conclusion has recently been arrived at in Vienna itself by Mattauch, Ehrenhaft's assistant, who has determined the densities of these slowly falling droplets, obtained by condensing mercury. He has determined these densities by measuring the rate of fall of the same particle at two or more different pressures in nitrogen, and has thus been able to make his computations independent of any use whatever of the charges carried by the drops. He, like myself, finds the densities of the most slowly falling of his drops to be

Fig. 2.



between 1 and 2, instead of 13.6. *These results, added to my own proof of the insensitivity of these drops to ultra-violet light, of course show definitely that these slowly falling particles are not solid spheres of mercury.* The precautions which both Wasser and I have taken to obtain pure mercury are really of no significance for these experiments: first, because chemical methods of purifying mean nothing when such minute quantities of oxides or other impurities as are required to coat a few sub-microscopic particles are concerned: and second, because, even if perfectly pure mercury be assumed, there is nothing at all to show that pure mercury may not in the process of condensing sometimes form into clusters of particles so small that they might be insensitive to light of longer wave-length than 1800 Å., such as Wasser and I have used. As Millikan has recently pointed out, the gaseous molecules of mercury have a long wave-length limit of about 1200 Å., while liquid mercury has its long wave-length limit

at 2735 Å. How large the aggregate must be before the latter limit is reached, no one knows.

My results agree with Wasser's in that the points in fig. 2 may be divided into three regions: in the first of these the drops show only normal effects in ultra-violet light; in the second region some drops are sensitive in ultra-violet light and others are not, or only slightly so; in the third region all drops are insensitive. We agree, also, in that the slightly sensitive or insensitive drops are the ones that yield apparent values of " $e$ " less than  $4.77 \times 10^{-10}$  E.S.U.

### VI. Value of the Constant $A$ for Hg.

The line drawn through those six points in fig. 2, which, from data on their behaviour in ultra-violet light, we conclude to be pure mercury, gives  $e = 4.77 \times 10^{-10}$ . The value of the correction constant  $A$  in Stokes's law when calculated from the slope of this line is .695, a value in very good agreement with that obtained by Derieux\*. This is of theoretical interest, as Millikan† has shown that in the generalized law of fall .7 is the lowest value that  $A$  can have, and corresponds to the case of diffuse reflexion of gas molecules from the surface of the drop. It is also the lowest value that has ever been obtained for any material or that theoretically can be obtained.

### VII. Summary.

The inverse photo-electric effect is a spurious effect, and is not due to discharge of positive electricity. This has been proved by careful work on oil, glycerine, and mercury drops in various gases. Work with mercury drops shows that the drops that yield values of " $e$ " smaller than  $4.77 \times 10^{-10}$  E.S.U. also show an abnormal behaviour to ultra-violet light—that is, they are only slightly sensitive or not sensitive at all.

The multiple relationship holds for the charges on these insensitive drops, proving that their charges are electronic, and that it is erroneous to assume their density to be that of mercury.

Drops that are known to be pure mercury satisfy Millikan's  $e_1^{23}$ ,  $1/pa$  relation, and yield  $4.77 \times 10^{-10}$  E.S.U. for the electronic charge, and .695 as the value of the correction constant,  $A$ , in Stokes's law.

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California Institute of Technology, Pasadena.

August 6, 1925.

\* Derieux, *Phys. Rev.* xi. (1918).

† Millikan, *loc. cit.*

XLII. *The Solubility of Hydrogen in Tin and Aluminium at High Temperatures.* By L. L. BIRCUMSHAW, B.A., M.Sc., from the National Physical Laboratory\*.

A CONSIDERABLE amount of work has been recorded on the occlusion of gases by solid metals, chiefly the systems palladium-hydrogen and platinum-hydrogen, but, except by Sieverts and his collaborators (*Zeit. Phys. Chem.* lxxiii. p. 115, 1910; lxxiv. p. 277, 1910; lxxvii. p. 591, 1911), very little attention has been paid to an examination of the solubility of gases in metals in the liquid state. In the cases investigated where solubility occurred, Sieverts found in general that solubility increases regularly with rise of temperature, very rapidly in the region of the melting-point and then again regularly with further rise of temperature. This applies to hydrogen in nickel, iron, and copper, where the solubility was determined between 400° C. and 1600° C., and up to one and a half atmospheres pressure of the gas. An extremely important result obtained is that both for the solid and liquid state at a constant temperature the solubility is proportional to the square root of the pressure, but at pressures below 100 mm. deviations from this relation were found. The direct application to this result of the van't Hoff Nerst distribution law  $m = K\sqrt{P}$ , where  $m$  is the mass of gas dissolved, leads to the conclusion that the gas dissolves as atoms and not as molecules. This relation has also been found to hold for the solubility of oxygen in silver by Donnan and Shaw (*Jour. Soc. Chem. Ind.* xxix. p. 987, 1910), who verified it for eight different pressures of the gas at 1075° C. These authors call attention to an important point: the fact that the solubility follows this relation does not allow us to distinguish between the possibility of solution as oxygen atoms or as silver monoxide. Sieverts and Krumbahr (*loc. cit.*) found that for sulphur dioxide in liquid copper  $m = k\sqrt{P}$ , and considered it very surprising that the law was followed in this case. They pointed out the possibility of this law being characteristic for all metallic solutions of gases and that the usual explanation (*i.e.*, that the gas dissolves as atoms) may be incorrect. Stubbs, who studied the solubility of this gas in copper by observations of the depression of the freezing-point (*J. Chem. Soc.* lxxiv. p. 1445, 1913), explains his results as being due to the *partial* formation of oxide and sulphide

\* Communicated by the Director.

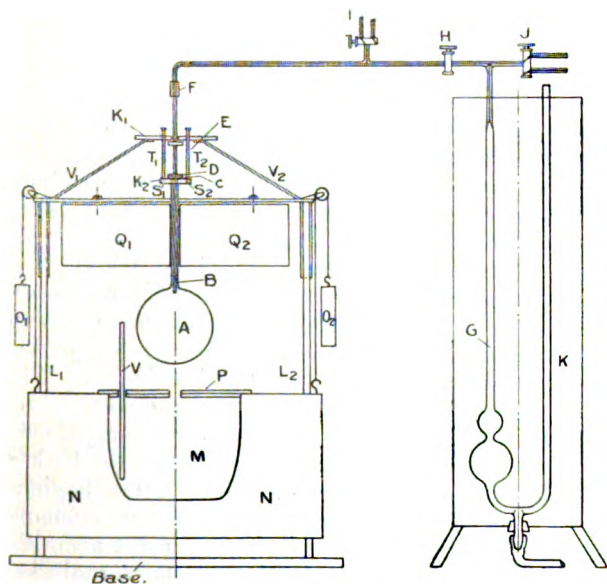
according to the following equation:  $6\text{Cu} + \text{SO}_2 = \text{Cu}_2\text{S} + 2\text{Cu}_2\text{O}$ . Sieverts found that hydrogen was quite insoluble in cadmium, thallium, zinc, lead, bismuth, tin, antimony, silver, gold, and aluminium, and that in the majority of cases where solubility occurred equilibrium was instantaneous.

The present work was undertaken with a view to investigating the absorption of different gases by a number of metals, especially aluminium, and it was first decided to verify Sieverts's observation on hydrogen and one of the metals of low melting-point—*e. g.*, tin.

### *Experimental.*

A diagram of the apparatus is shown in fig. 1. A is a

Fig. 1.



vitreous silica flask (capacity 100 c.c.) with a long neck terminating in a collar C, whose upper surface is ground flat. Into the neck of this flask fits the silica capillary rod B which carries two collars—D, whose lower surface has been ground to fit C, and another at E. B is fitted closely, by means of a short piece of pressure-tubing at F, to a capillary glass tube which connects the apparatus with a gas burette. The burette has a total capacity of 48.75 c.c. and is graduated with an arbitrary scale whose large divisions are equal to

0.6 c.c. approximately, and are divided into tenths. The burette was calibrated in the Metrology Department of the N.P.L., and by using a telescope 1/10 of a small division could be estimated. A two-way tap was fused in at H, a three-way tap at I made connexion to a pump and a McLeod gauge and served to fill the apparatus with air when necessary. Another three-way tap was fused on to the other side of the burette (which was contained in the water-jacket K). This tap served to fill the apparatus with gas. The flask was held in position between the metal rings  $K_1$ ,  $K_2$ , a thin rubber washer being interposed between each ring and the collar of the rod, C and D were held together with the necessary tightness by means of the screws ( $S_1$ ,  $S_2$ ,  $S_3$ ) in the connecting rods ( $T_1$ ,  $T_2$ ,  $T_3$ ). The ring  $K_1$  was firmly attached to the vertical supports of the furnace by the steel strips ( $V_1$ ,  $V_2$ ,  $V_3$ ). The heating was conducted in a bath of molten tin M contained in a salamander pot wound with nichrome wire and heated electrically. The pot, lagged with magnesia packing, was fixed into the furnace box N, which contained three iron tubes through which fitted loosely the supports  $L_1$ ,  $L_2$ ,  $L_3$ . By means of the counter weights ( $O_1$ ,  $O_2$ ), N could be drawn up and fixed in any position. When the flask was immersed in the metal bath, two copper water-coolers ( $Q_1$ ,  $Q_2$ ), shaped to fit closely round the neck of the flask, rested on the "Mabor" plate P which covered the pot. Good metallic contact between the coolers and the neck of the flask was made with thin copper-foil. The silica thermocouple tube V passed through a narrow tube in one of the coolers, so adjusted as to fit exactly over a small hole in the "Mabor" plate. Nitrogen was passed slowly above the surface of the metal through a similar tube in the other cooler to prevent the rapid oxidation of the tin which otherwise occurred. When the flask was in the bath it was immersed to a point above the beginning of the narrow neck. Before each experiment was commenced, the level of molten tin in the pot was adjusted accurately by means of a steel point suspended from a horizontal steel grip placed flat on the horizontal top of the furnace. The ground joint D-C and the joint at F were made gas-tight by means of a little sealing-wax varnish, and water was passed through the coolers from a constant head to ensure a constant temperature gradient between the bulb and the neck.

The principle of the method employed was extremely simple. The volume of gas required to fill the flask at any given temperature was determined. A known weight of metal was then introduced and the volume of gas required to fill the flask again determined. From these data and the density of the metal at that temperature the volume of gas

absorbed was calculated, for if  $V_c$  is the calibration volume of the flask,  $V_D$  the volume required to fill the flask when containing the metal, and  $V_M$  the volume of metal at that particular temperature (all volumes being, of course, reduced to  $0^\circ\text{C}.$ ), then the volume of gas absorbed is  $(V_D + V_M) - V_c$ . The hydrogen used was prepared by the electrolysis of 5 per cent. sodium hydroxide solution, and was freed from traces of oxygen by passing the gas over silica chips at  $500^\circ\text{C}.$  and afterwards drying.

The calibration was made in the following manner: After the flask had been immersed in the furnace for some time and a constant temperature attained, the flask and capillary up to the tap H were exhausted through I. The burette was filled with gas by lowering the mercury until it just sealed the junction between the burette and levelling tube. Hydrogen was then bubbled through from J for half an hour, when the latter was turned and the mercury levelled. One operator then carefully opened the tap H, allowing the gas to flow over into the evacuated flask, while another gradually raised the mercury in the burette. The mercury was then levelled and read, and the temperature of the water-jacket noted. It was found that the volume determined in this way could be repeated usually to 0.05 c.o., and the tightness of the apparatus was tested by allowing the gas to remain in the flask for some time when no alteration of the level of the mercury could be detected. In some cases this was continued for two hours. The whole process was then repeated with a known weight of metal in the flask.

#### *Tin-Hydrogen.*

Experiments were first made at  $306^\circ\text{C}.$  The metal used contained 0.13 per cent. of impurities which consisted of As 0.04 per cent., Pb 0.02 per cent., Cu 0.02 per cent., Fe 0.01 per cent., Ni 0.02 per cent., Zn 0.02 per cent. It was just melted, skimmed, and poured into the weighed flask. The metal in the flask weighed 579.1 grams. It was heated *in vacuo*, pumping being continued all the time, and allowed to cool, this treatment being repeated the next day. Hydrogen (purified and dry) was then admitted in the manner described above. The time and burette readings are given below:—

Time	Burette-reading.	Temperature of water-jacket.
3.9	31.54	$18.0^\circ\text{C}.$
3.14	31.54	"
3.30	31.52	"
4.0	31.50	"
5.15	31.50	$18.1^\circ$

The division 31.50 on the burette corresponds with a reading of 20.60 c.c., the initial volume of gas 28.72 c.c.,  $V_D = 7.68$  c.c. The calibration volume of the flask was 53.85 c.c., and the reduced volume occupied by the metal was 46.25. The density of tin at 306° C. was taken as 6.96, the mean of the values given by Pascal and Jouniaux (*Comptes Rendus*, clviii. p. 415, 1914) and Day and Sosman (*Amer. J. Science*, p. 10, 1914), so we have

$$(V_D + V_M) - V_C = 0.07 \text{ c.c.}$$

In another experiment made in another flask at the same temperature 723.7 grams of metal were used. Initial volume of gas in burette 28.72 c.c.:—

Time.	Burette-reading.	Temperature of water-jacket.
2.42	34.10	18.0° C.
4.42	34.00	18.8°

34.00 corresponds with a volume of 22.09 c.c. so that  $V_D = 6.22$  c.c.,  $V_M = 49.21$  c.c., and  $V_C$  in this case 55.38 c.c., hence  $V_D + V_M - V_C = 0.05$  c.c. Both of these results are well within the possible error of a determination, so it was concluded that the solubility of hydrogen in tin at this temperature is extremely small.

Experiments were next made at a temperature of 800° C. The weight of metal taken was 437.9 grams, and it was heated at 800° C. *in vacuo* for about 12 hours, which included 2 hours at 800° C. Hydrogen was then introduced and the rate of absorption of gas is given in the following table:—

Time.	Burette-reading.	Temperature of water-jacket.
2.20	18.81	20.9° C.
2.35	18.20	21.0
2.45	17.91	21.1
3.0	17.60	21.3
3.30	17.15	21.7
4.10	16.70	22.2
5.10	16.30	22.7
6.10	16.05	22.9

Mean Barometer: 747.7 mm.

The final reading in the burette 16.05 corrected to the initial temperature 20.9° C. corresponds with a volume  $V_D$  of 16.02 c.c., and the corrected volume of the metal is 16.83 c.c. The mean calibration value of the flask was 31.31 c.c., so that the gas dissolved was 1.51 c.c. (N.T.P.). The density of tin at 800° C. was taken as 6.62, the mean between the value

given by Day and Sosman (Amer. J. Science, p. 10, 1914) and Bornemann and Sauerwald (*Zeit. f. Metallkunde*, xiv. p. 145, 1922).

The metal from the previous experiment was heated in *vacuo* for about 12 hours (including two hours at 800° C.) and hydrogen introduced again :—

Time.	Burette-reading.	Temperature of water-jacket.
12.50	19.00	18.8° C.
1.2	18.52	19.0
1.17	18.20	19.1
2.5	17.90	19.6
2.30	17.60	19.9
3.0	17.50	20.0
3.45	17.31	20.3
4.15	17.20	20.8
4.45	17.10	21.0

Mean Barometer: 763.3 mm.

Here  $V_D$  is 15.58 c.c., so that the gas dissolved is 1.10 c.c. (N.T.P.).

The metal was again subjected to the same treatment, heating in *vacuo* for about 12 hours including two hours at 800° C., and hydrogen introduced once more :—

Time.	Burette-reading.	Temperature of water-jacket.
12.45	18.52	22.0° C.
1.2	18.00	22.4
2.20	17.60	23.8
2.50	17.40	24.2
3.50	17.20	25.0
4.20	17.11	25.1
5.0	17.00	25.4

$V_D$  is 15.50 c.c. and the gas dissolved is 1.01 c.c. N.T.P. These experiments were continued until the absorption was of the order of one-tenth of a c.c. per hour, and the results are shown graphically in fig. 2. It is practically certain that the point 0 is not the true origin for curves II. and III., i.e., the time of heating after experiment 1 was insufficient to remove all the gas from the metal. It will be seen that saturation has not been reached.

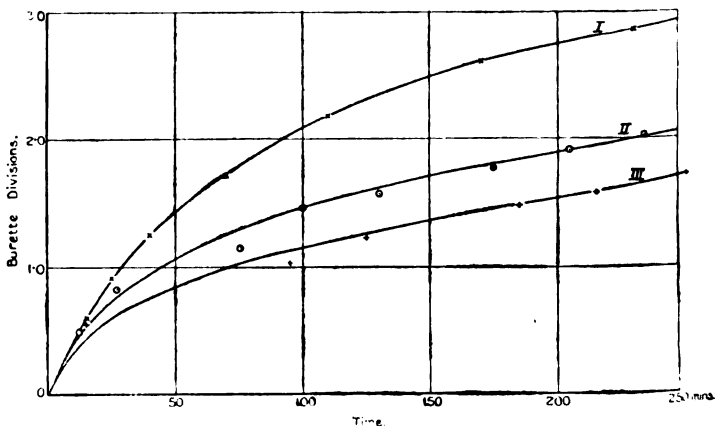
Adeney and Becker (Scient. Proc. Roy. Soc. Dub. xv. p. 385) in an investigation on the rate of solution of several gases in water and salt solution found the relation

$w = \frac{a}{b} - ce^{-bt}$ , where  $w$  is the amount of gas dissolved at time  $t$  and  $a$ ,  $b$ , and  $c$  are constants. From this it follows that



$dw/dt$  plotted against  $w$  should be a straight line. This formula is developed on the assumption that the liquid is well stirred, *i. e.*, at any moment there are no concentration gradients of gas in the liquid. It was conceivable that there might be sufficient convection in the molten metal to approximate to this relation. The tangent-derived curve from I. (fig. 2), plotted against  $w$ , is shown in fig. 3, and it will be seen that a well-marked curve is obtained.

Fig. 2.



There is the possibility that the process is governed by the diffusion of the gas through the metal. In this case the rate of absorption should be determined by Ficks's well-known law,

$$\frac{\partial w}{\partial t} = k \left( \frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2} \right).$$

If we assume that diffusion takes place from an infinitely thin saturated layer on the surface the problem approximates to the case cited by Mellor (*Higher Mathematics*, p. 489, problem 5), in which a cylinder containing a saturated salt solution is immersed in pure water, and we may assume that the solution will be of the same form except that the constants will be chosen to satisfy the new boundary condition, *viz.* :

$$\text{when } x=0, \quad w=w_0 \text{ a constant,}$$

$$\text{when } r=a, \quad \frac{\partial w}{\partial r} = 0,$$

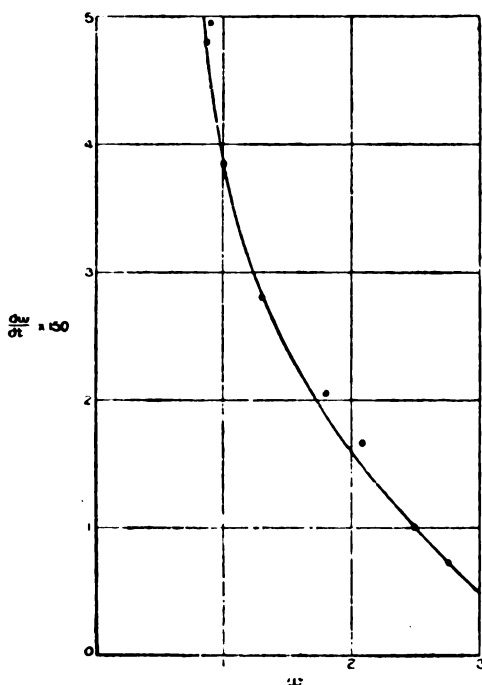
for all values of  $t$ . If  $w$  is the volume of gas dissolved, the equation will be of the form

$$w = A + Be^{-\alpha t} + Ce^{-\beta \alpha t} + \dots,$$

where  $A$ ,  $B$ ,  $C$ , and  $\alpha$  are constants. If we neglect the last term on the right-hand side of this equation, differentiate  $w$  with regard to  $t$ , and substitute for  $B$ , we get

$$\frac{\partial w}{\partial t} = -\alpha(w - A).$$

Fig. 3.



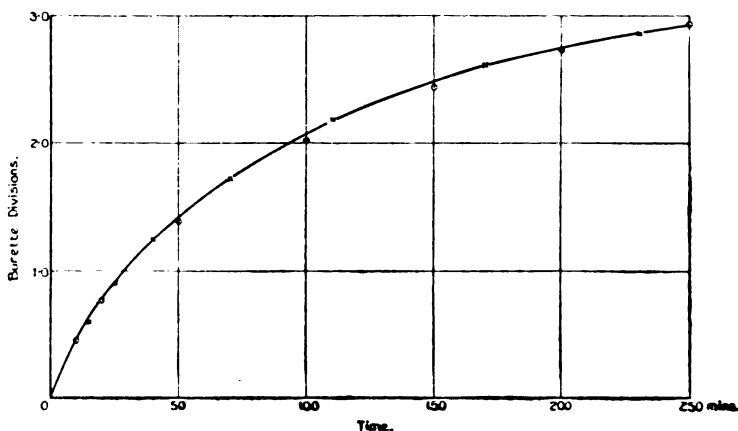
A value for  $\alpha$  is obtained in this way from the lower part of the curve shown in fig. 3, where the term  $Ce^{-\beta \alpha t}$  is negligible. The final equation assumes this form

$$w = 3.38 - 2.86e^{-0.0074t} - 0.52e^{-0.066t}.$$

In fig. 4 the curve I. from fig. 2 is reproduced and the points  $\odot$  are values calculated from the above equation. When  $t$  is infinite  $w=3.38$ , and this is the saturation value and corresponds with a solubility of 4.19 c.c. N.T.P. per kilogram of metal.

Since the completion of the above work a paper has appeared on the solubility of oxygen in silver (N. Parravano and G. Malquori, *Atti R. Acad.* vi. 1, p. 417, 1925). These authors come to the conclusion that the velocity of absorption of the gas is a function of the velocity with which the gas diffuses into the interior of the metal.

Fig. 4.



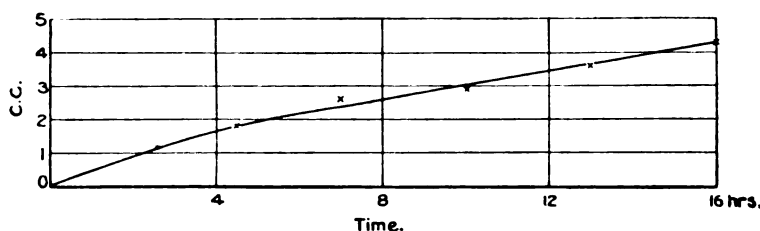
### *Experiments on Aluminium.*

Great difficulty was experienced, owing to the attack on the silica vessel by the metal. It was found that whenever the flask was filled with molten metal the freezing of the latter always led to the breaking of the flask. An attempt was made to use a fine film of some protective coating, and the best results were obtained with a mixture which consisted of 7.5 grams of pure alumina and 7.0 grams of china-clay made into a fine cream with 25 c.c. of water. A few c.c. of this mixture were pipetted into the flask, which was rapidly rotated and gently warmed until a very fine even coating was obtained, and the flask was then heated for a time to 1100° C.

A preliminary experiment showed the metal to contain a

certain amount of gas. 125.3 grams of aluminium\* were heated *in vacuo* for 109 hours at 800° C. and 19.45 c.c. of gas obtained. On analysis this gas was found to contain 82.30 per cent. of hydrogen. Carbon monoxide, carbon dioxide, and oxygen were found to be absent. Heated for another five hours a further quantity of 1.7 c.c. of gas was obtained which contained 75 per cent. of hydrogen; the rest of the gas in these experiments appeared to be nitrogen. It was found to be almost impossible to keep the apparatus absolutely tight for such long periods of time, but tests made on the apparatus before and after the experiment showed that the total leak would account for about 0.8 c.c. of nitrogen, so that it is extremely probable that some of this gas is actually evolved on heating the metal. Guichard and Jourdain (*Comptes Rendus*, clv. p. 160, 1912) obtained from a sample of aluminium a quantity of gas which contained 10 per cent. of nitrogen.

Fig. 5.



Owing to two breakdowns of the furnace it was not possible to determine the rate of evolution of the gas over the whole period of heating, but it is shown for the first sixteen hours in I (fig. 5). It will be seen that the rate of evolution is practically linear after the first four hours, but the accuracy of these observations is not very high.

At this stage it was quite obvious that there still remained a considerable quantity of gas in the metal, but, owing to the probability of the metal getting through the protective coating on the flask, it was decided to attempt to obtain a very approximate value for the solubility. Pure hydrogen was therefore introduced and the following observations were recorded. The temperature of the metal was 670° C.

\* The aluminium contained 0.21 per cent. of silicon and 0.17 per cent. of iron.

## 520 Mr. L. L. Bircumshaw on the Solubility of Hydrogen

Time.	Burette reading.	Temperature of water-jacket.
1.50 P.M.	10.56	19.1° C.
2.0	10.05	19.6
2.30	9.40	19.8
3.30	9.32	20.1
4.30	8.94	20.5
5.30	8.73	21.0
6.30	8.64	21.2
7.30	8.50	21.4
8.30	8.44	20.8
9.0	8.38	20.4
9.30	8.22	20.2
10.30	8.08	20.0
11.30	7.89	20.3
12.40 A.M.	7.77	21.0
2.0	7.65	22.1
3.30	7.54	22.3
5.0	7.40	21.8
6.30	7.25	21.9
8.0	7.12	22.7
9.30	7.02	23.0
10.30	6.93	22.9

Mean Barometer : 767.9 mm.

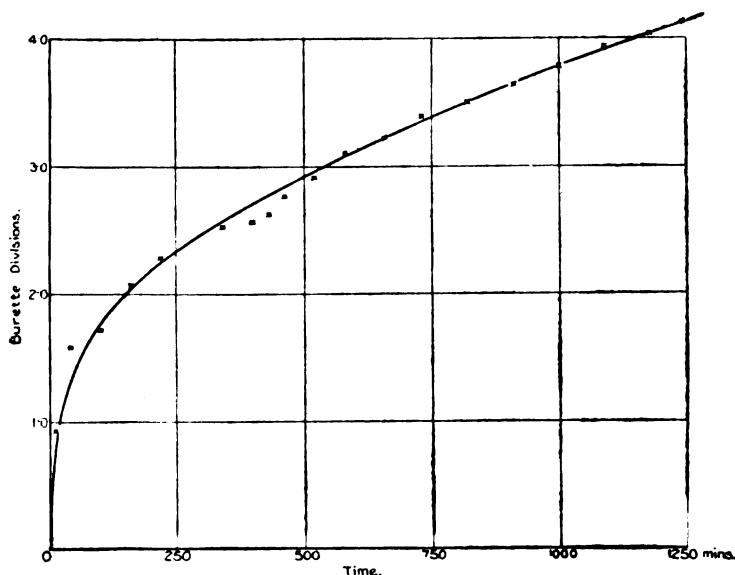
The density of aluminium at 670° C. was taken as 2.378 (Edwards and Moorman, Chem. and Met. Eng. xxiv. p. 61, 1921), and calculation showed that before the first reading was taken, 0.24 c.c. of gas had entered the metal. This corresponds with 0.40 burette-divisions. These results (corrected for the immediate absorption 0.4) are shown graphically in fig. 6. The rate at which gas is being absorbed at the end of the experiment is of the order of 0.05 c.c. per hour ; nevertheless, it is readily seen from the curve that even after this time (20 hours) the metal is apparently far from saturated. The final measurement (at 10.30 A.M.) corresponds with a solubility of 18.67 c.c. (N.T.P.) per kilogram.

The metal was frozen in hydrogen and cooled, the residual gas pumped off cold, and the metal once more heated to 670° C. for a period of 20 hours. 2.36 c.c. of gas were obtained, which analysis showed to contain 2.0 c.c. of hydrogen. The amount of gas which in the previous experiment had been absorbed during this time was 2.34 c.c. In this case, then, practically the same amount of gas which is absorbed in a certain time is given off on heating *in vacuo* for the same time, but it is extremely probable that in this case we are dealing with a relatively thin layer of the metal.

One important point which arises from these experiments

is the very long duration of heating *in vacuo* which appears to be necessary to expel the dissolved gas from a metal. In the case of aluminium mentioned above, after 114 hours gas was still coming off. If we consider the formation of a spherical bubble of radius  $r$  in the interior of a metal of density  $\rho$  at a depth  $h$  cm. below the surface, then, if  $T$  is the surface-tension of the metal, a pressure  $\left(h\rho g + \frac{2T}{r}\right)$

Fig. 6.



dynes/cm.<sup>2</sup> must be exceeded in the bubble before it can grow. When the bubbles are very small, of course, the term  $\frac{2T}{r}$  becomes considerable, and for a minute bubble forming in a metal its value may be from five to ten times greater than in the case of a bubble of the same size forming in water. The suggestion is put forward that the difficulty of removing the gas dissolved in a metal is due to the relatively high surface-tension of the medium in which the gas bubbles are formed.

W. C. McC. Lewis (Journ. Chem. Soc. cxvii. p. 623, 1920) has put forward the theory that the ability of a metal to dissolve gas depends on the ability of the metal to dissociate the gas, and he calculates the critical increment of dissociation per gram mol. of hydrogen in the case of a number of metals.

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For pure hydrogen in contact with a metal we have from mass-action considerations  $k_1 = \frac{[H]^2}{[H_2]}$  in the gas phase, and

also a further equilibrium  $k_2 = \frac{[H]}{[H_M]}$  between the atomic

hydrogen in the gas phase and the metal. Presumably hydrogen is dissociated in the surface-layer, and diffusion of the atoms takes place until their concentration in the metal is uniform. On these assumptions the most probable mechanism of the removal of gas in the absence of nuclei and bubble formation would be the diffusion of the atoms to the surface where re-combination into molecules takes place. In this case the rate of absorption of gas by a metal should be equal to the rate of evolution when the metal is heated at the same temperature *in vacuo*.

An apparatus for the investigation of the solubilities of gases in metals has now been designed and constructed in which the gas can be bubbled through the molten metal, and further experiments are now being made.

### *Summary.*

It appears to be practically impossible to saturate a metal with a gas by keeping the unstirred metal at constant temperature in contact with the gas, owing to the long time necessary for the attainment of equilibrium.

The statement of Sieverts that hydrogen is insoluble in tin and aluminium has not been verified. A small but definite solubility of hydrogen in tin at 800° C. has been measured, and evidence of a considerable solubility of hydrogen in aluminium just above its melting-point has been found.

The rate of solution of hydrogen in tin is determined by the rate of diffusion of gas through the bulk of the metal.

Very long times appear to be necessary to remove all the gas from a metal by heating *in vacuo*, and suggestions are made to explain this fact.

The author would like to thank Dr. W. Rosenhain, F.R.S., for his interest and advice during the progress of this work; Mr. L. F. G. Simmons, B.A., for assistance in obtaining the equation to the curve I (fig. 2), and Mr. J. Trotter for assistance in the experimental part of the work.

### XLIII. *Energy in the Earth's Atmosphere.*

By D. BRUNT, M.A., B.Sc.\*

#### 1. *The Kinetic Energy of the Atmosphere* †.

**I**F we take the parallels of 30° North and South as separating the main Easterly and Westerly circulations of the atmosphere, the Easterly belt, covering a range of 60° in latitude, will contain half the mass of the atmosphere. Assuming the average pressure to be one atmosphere, we can readily deduce an approximate value of  $2.7 \times 10^{21}$  grammes, or  $2.7 \times 10^{15}$  metric tons. Taking the mean velocity to be 10 metres/second, a value which is in agreement with the distribution of pressure, we find the kinetic energy of the equatorial belt to be

$$\frac{1}{2} 2.7 \times 10^{21} \times 10^6 \text{ ergs} = 1.35 \times 10^{27} \text{ ergs.}$$

The combined masses of the polar caps will not differ appreciably from the mass of the equatorial belt, and the moment of momentum of the two circulations should balance, since they are produced by internal reactions within the earth's atmosphere. The equality of moments of momentum demands that the Westerly velocity should be the greater, and the energy of the combined polar caps should exceed somewhat that of the equatorial belt.

It appears safe to assume that the total kinetic energy of the earth's atmosphere is of the order of  $3 \times 10^{27}$  ergs.

This estimate does not specifically include the energy of the circulations around cyclones and anticyclones. An estimate has been given by Sir Napier Shaw of the kinetic energy of a cyclone which formed over the lower part of the North Sea between July 27th and August 3rd, 1917, which incidentally ruined an allied offensive movement in Flanders. This depression was apparently formed *in situ*, and filled up *in situ*. Its diameter was about 1400 km. and the depth at the centre was 10 millibars. The kinetic energy developed was  $1.5 \times 10^{24}$  ergs.

If the kinetic energy of the earth's atmosphere, roughly computed above, were spread uniformly over the earth's

\* Communicated by the Director of the Meteorological Office, Air Ministry. This paper is a slight expansion of a paper communicated to the British Association in 1923.

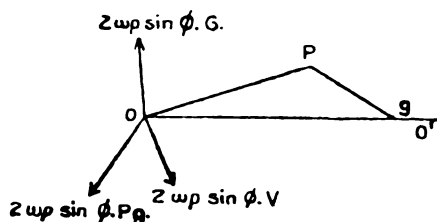
† This section follows the lines of a discussion by Sir Napier Shaw in the 'Dictionary of Applied Physics,' vol. iii. p. 67.



surface, the amount contained in the portion of the atmosphere over a circle of diameter 1400 km. would be  $10^{24}$  ergs, so that in the case considered the kinetic energy of the cyclone was about 50 per cent. higher than the average kinetic energy of the general circulation.

## 2. *The Dissipation of Energy by Turbulence.*

The kinetic energy of the atmosphere is subject to a continual dissipation due to the effect of turbulence. It is proposed to estimate the amount of this dissipation. The notation used by the present writer in a paper on "Internal Friction in the Earth's Atmosphere" \* will be used. Consider the conditions holding at a point O at a height  $z$ . Let  $OO'$  be the tangent to the isobar, and let  $Og$  denote the



velocity of the geostrophic wind  $G$ . Let  $OP$  denote the actual wind, of velocity  $V$ . The diagram is drawn in a horizontal plane.

Consider now the forces acting on an element of air at  $O$ . It is acted upon by

- (a) The pressure gradient of magnitude  $2\omega p \sin \phi . G$ , acting in a direction perpendicular to  $Oq$ ;
- (b) The "deviating force" due to the earth's rotation, of magnitude  $2\omega p \sin \phi . V$ , acting at right angles to  $OP$ . Here  $\phi$  is the latitude, and  $\omega$  the angular velocity of the earth; and
- (c) The effect of turbulence in producing a loss or gain of momentum. This effect may be assimilated to a viscous force, and is the "internal friction" of Ekman. Let the magnitude of this force be  $R$ .

If the motion is steady the three factors (a), (b), and (c) must balance. It follows then, from the triangle of forces, that  $R$  must be of magnitude  $2\omega p \sin \phi \times Pg$ , and must act in a direction at right angles to  $Pg$ .

\* Q. J. Roy. Met. Soc. April 1920.

The rate at which work is done by the force  $R$  is equal to the product of  $R$  and the component of velocity along the direction of  $R$  ( $\perp$  to  $gP$ ). This amounts to

$$\begin{aligned} OP \sin OPg \times R &= 2\omega\rho \sin \phi Pg \times OP \sin OPg \\ &= 4\omega\rho \sin \phi \times \text{area of triangle } OgP \\ &= 2\omega\rho \sin \phi Og \times OP \sin POg \\ &= 2\omega\rho \sin \phi G \times OP \sin POg. \end{aligned}$$

If we take the axis of  $x$  along  $OO'$ , the axis of  $y$  perpendicular to this, and let  $u$  and  $v$  be the component velocities along the axes of  $x$  and  $y$ , then the rate of dissipation of energy  $= -v \frac{\partial p}{\partial y}$ .

When the steady motion is along the isobar, or  $v=0$ , there is no dissipation of energy. If the motion is across the isobars into the low pressure, there is a dissipation of energy, and steady motion can only be maintained by supplying energy at a rate equal to the product of velocity of inflow and gradient of pressure.

The total dissipation of energy of the main current in a vertical cylinder of unit cross-section extending from the ground to the top of the atmosphere is

$$-\int_0^{\infty} v \frac{\partial p}{\partial y} dz.$$

This expression can be integrated if the distribution of velocity and of pressure is known at all heights.

G. I. Taylor deduced the law of variation of wind with height in the atmosphere in the case where the coefficient of eddy diffusion  $K$  remains constant at all heights. In the diagram let  $Og$  denote the geostrophic wind in magnitude and direction, let  $OP$  or  $V$  denote the wind at height  $z$  above the ground \*, and let  $\alpha$  be the angle between the direction of the surface wind and the isobar. Then if we introduce a new constant  $B$ , defined by

$$B^2 = \omega \sin \phi / K,$$

where  $\omega$  is the angular velocity of the earth, and  $\phi$  the latitude, we may write the relation between  $V$  and the height  $z$  in the form

$$V = G + \sqrt{2} G \sin \alpha e^{-Bz + i(3\pi/4 + \alpha - Bz)}.$$

$$* \text{ i. e. } V = u + iv.$$

The geostrophic wind  $G$  is assumed to be constant in the deduction of this equation. Both  $G$  and the density  $\rho$  will be treated as constant in what follows. We then have

$$\begin{aligned} -v \frac{\partial p}{\partial y} &= v \times 2\omega\rho \sin \phi \cdot G \\ &= \text{imaginary part of } V \times 2\omega\rho \sin \phi \cdot G \\ &= \text{imaginary part of} \\ &\quad 2\sqrt{2}\omega\rho \sin \phi \sin \alpha G^2 \int_0^z e^{-Bz+i(3\pi/4+\alpha-Bz)} dz \\ &= 2\omega\rho \sin \phi \sin \alpha \frac{G^2}{B} \left[ e^{-Bz} \cos(\alpha - Bz) \right]_0^z. \end{aligned}$$

The total loss of energy in the column extending from the ground to the top of the atmosphere, assuming the same law of distribution of wind to hold, would be

$$2\omega\rho \sin \phi \sin \alpha \cos \alpha G^2/B.$$

The total loss from the ground up to the height at which the wind direction attains the direction of the tangent to the isobar, a height defined by  $Bz = 3\pi/4 + \alpha$ , is

$$2\omega\rho \sin \phi \sin \alpha \frac{G^2}{B} \left\{ \cos \alpha - \frac{1}{\sqrt{2}} e^{-(3\pi/4+\alpha)} \right\}.$$

The second term inside the bracket is small by comparison with the first, so that the loss of energy up to the height

$$z = (3\pi/4 + \alpha)/B$$

is approximately

$$2\omega\rho \sin \phi \sin \alpha \cos \alpha G^2/B,$$

which is the total loss in the whole column extending to the top of the atmosphere. Thus with the assumed wind distribution the dissipation of energy by turbulence is effectively restricted to the layer below that at which the wind direction first attains the direction of the tangent to the isobar.

As a very rough estimate of the total amount of energy contained within this layer, we may take

$$\frac{1}{2}\rho G^2(3\pi/4 + \alpha)/B, \text{ or even } \frac{1}{2}\rho G^2\pi/B,$$

with a sufficient degree of accuracy.

The fraction of energy lost per second

$$= 4\omega \sin \phi \sin \alpha \cos \alpha / \pi.$$

The fraction of energy lost per day

$$= 4 \sin \phi \sin 2\alpha.$$

If we take

$$\sin \phi = 0.6, \quad \alpha = 22\frac{1}{2}^\circ, \quad \text{or} \quad \sin 2\alpha = \frac{1}{\sqrt{2}},$$

then

$$4 \sin \phi \sin 2\alpha = 1.68,$$

so that if the loss of energy were maintained at the same rate, the kinetic energy of the main current in the layer we are considering would be destroyed in a little over 14 hours.

In order to obtain some idea of the actual amount of kinetic energy destroyed by turbulence in a given time, we shall assume

$$G = 15 \text{ metres/sec.}, \quad \alpha = 22\frac{1}{2}^\circ, \quad B = 3 \cdot 10^{-5},$$

corresponding to

$$K = 5 \cdot 10^4, \quad \sin \phi = 0.6, \quad \text{and} \quad \rho = 1.2 \cdot 10^{-3} \text{ grams/cm.}^3$$

Then the rate of loss of kinetic energy in the column disturbed by turbulence due to the ground

$$\begin{aligned} &= 2\omega\rho \sin \phi G^2 \sin \alpha \cos \alpha / B \\ &= 3 \cdot 10^8 \text{ ergs sec./cm.}^2 \\ &= 3 \cdot 10^{-3} \text{ kilowatts/(metre)}^2. \end{aligned}$$

With the wind distribution assumed above, the loss of kinetic energy through turbulence becomes negligible above the height at which the gradient wind direction is first attained. This height is given by

$$z = (3\pi/4 + \alpha)/B,$$

and if  $B$  be assumed to be  $3 \cdot 10^{-5}$  this height is about 1 kilometre.

At greater heights, the changes of wind with height are determined, not by turbulence produced at the ground, but by the horizontal distribution of temperature. An examination of recorded wind distribution is necessary.

The rate of loss of energy

$$= K\rho \left\{ u \frac{\partial^2 u}{\partial z^2} + v \frac{\partial^2 v}{\partial z^2} \right\},$$

or in terms of finite differences

$$= K\rho \left\{ u \frac{\Delta}{\Delta z} \cdot \frac{\Delta u}{\Delta z} + v \frac{\Delta}{\Delta z} \frac{\Delta v}{\Delta z} \right\}.$$

A number of sample cases when conditions were relatively steady were worked out, showing that at 3 km. the term

$$u \frac{\partial^2 u}{\partial z^2} + v \frac{\partial^2 v}{\partial z^2}$$

is of the order of  $2 \cdot 10^{-4}$  to  $3 \cdot 10^{-4}$ , while at 10 km. it is of the order of  $\frac{1}{2} \cdot 10^{-4}$  to  $1 \cdot 10^{-4}$ . We shall therefore assume, as a rough average value from 1 to 10 km., that

$$u \frac{\partial^2 u}{\partial z^2} + v \frac{\partial^2 v}{\partial z^2} = 2 \cdot 10^{-4}.$$

At the ground  $K\rho = 5 \cdot 10^4 \times 1 \cdot 3 \cdot 10^{-3} = 65$ .

At 5 km.  $K\rho = 5 \cdot 10^3 \times 7 \cdot 10^{-4} = 3 \cdot 5$ .

$K\rho$  thus decreases rapidly with height in the troposphere, and the average value of

$$K\rho \left( u \frac{\partial^2 u}{\partial z^2} + v \frac{\partial^2 v}{\partial z^2} \right)$$

is of the order of  $2 \cdot 10^{-3}$  ergs per sec. per cm.<sup>3</sup>

=  $18 \cdot 10^6$  ergs per sec. per metre<sup>2</sup> of the earth's surface,

=  $1 \cdot 8 \cdot 10^{-3}$  kilowatts per metre<sup>2</sup>.

Above 10 kilometres the value of

$$u \frac{\partial^2 u}{\partial z^2} + v \frac{\partial^2 v}{\partial z^2}$$

is small except at the base of the stratosphere. No data are available for the estimation of the dissipation of energy at this level, but no very considerable error can arise if we neglect the dissipation above 10 kilometres. We then have for the dissipation above 1 square metre of the earth's surface :

From the ground to 1 km. ...  $3 \cdot 10^{-3}$  kilowatts per metre<sup>2</sup>.

From 1 km. to 10 km. ....  $2 \cdot 10^{-3}$      "     "     "

Total .....  $5 \cdot 10^{-3}$      "     "     "

This total is the rate at which the kinetic energy of the earth's atmosphere is being dissipated by turbulence. It is probably an overestimate for those regions of the earth's

atmosphere in which the winds are normally light at all heights, but so far as order of magnitude is concerned it may be accepted with a fair degree of faith, in spite of the numerous approximations made. On the whole it appears likely to be an overestimate rather than an underestimate.

The total energy above one square metre of the earth's surface, on the assumption of uniform velocity of 10 metres/sec., =  $5 \cdot 10^{12}$  ergs. The rate of dissipation by turbulence =  $5 \cdot 10^7$  ergs per metre<sup>2</sup> per sec. Hence, if the same rate of dissipation were maintained for  $10^5$  seconds, or  $1\frac{1}{2}$  days, the whole kinetic energy would be destroyed in that time. If the rate of dissipation is assumed to be proportional to the total kinetic energy, then the total kinetic energy would be reduced to one-tenth its original value in three days. As no sensible change takes place in the kinetic energy of the general circulation of the atmosphere, we conclude that the loss by turbulence is being continually made up by the conversion of solar energy into kinetic energy.

The expression which gives the relation between the wind  $V$  and the height  $z$  demands that the wind should increase with height, eventually surpassing the magnitude of the geostrophic wind  $G$ , and through a considerable layer whose thickness should exceed  $\frac{1}{2}$  km. the wind velocity should everywhere exceed the geostrophic wind  $G$ . If the earth's surface were everywhere flat and smooth, so that no turbulence could originate at its surface, we should expect to find the wind at all heights equal to the geostrophic wind, at any rate for straight isobars. But when the hypothetical smooth earth is replaced by the irregular surface of the earth as we know it, the wind velocity is decreased in the lowest layers, and increased in a higher layer. It is difficult to conceive of the physical mechanism which could bring this about. Is it analogous to a wheel spinning freely about a horizontal axis? In this case, when the wheel is free of all constraints at its periphery, and spins about its centre, every point is moving with the same velocity. But if the wheel is made to rotate in contact with a rough surface, the part in contact with the surface is instantaneously at rest, and the topmost point of the wheel has its velocity doubled. The difficulty of understanding the somewhat analogous motion in the atmosphere is largely due to the difficulty of drawing a mental picture of the behaviour of an individual eddy.

### 3. *Comparison of the Eddy-Dissipation of Kinetic Energy with the Radiation coming in from the Sun.*

The value of the solar constant being taken as 2 gramme calories per cm.<sup>2</sup> per minute, then the amount of radiation coming from the sun into the earth's atmosphere

$$\begin{aligned}
 &= 2 \text{ g. cal. per cm.}^2 \text{ per min.} = 8.36 \text{ joules per cm.}^2 \text{ per min.} \\
 &= 83600 \text{ joules per metre}^2 \text{ per min.} \\
 &= 1400 \text{ joules per metre}^2 \text{ per sec.} \\
 &= 1400 \text{ watts per metre}^2. \\
 &= 1.4 \text{ kilowatts per metre}^2.
 \end{aligned}$$

But the radiation intercepted by the earth is the portion of the beam of solar radiation intercepted by an area  $\pi r^2$ , where  $r$  is the radius of the earth. This is spread over the whole area of the earth  $4\pi r^2$ , and hence the effective incoming radiation per metre<sup>2</sup> is one-fourth of the figure given above, and amounts to 0.35 kilowatt per metre<sup>2</sup>.

Also Abbot and Fowle estimate that the effect of reflexion from the earth's surface and from clouds is to reduce by 37 per cent. the amount of solar radiation available for absorption and subsequent conversion into kinetic energy. The effective incoming solar radiation is therefore 0.22 kilowatts per metre<sup>2</sup>, when averaged over the whole of the earth's surface.

The rate of dissipation by turbulence was given above as  $5 \cdot 10^{-3}$  kilowatts per metre<sup>2</sup>, which is only a little over 2 per cent. of the effective incoming solar radiation.

Thus the conversion of a little over 2 per cent. of the incoming solar radiation into kinetic energy will suffice to make up for the dissipation by turbulence.

### 4. *The means of Conversion of Solar Energy into Kinetic Energy.*

No universally acceptable theory has been put forward to explain the mechanism of conversion of solar energy into kinetic energy.

Sir Napier Shaw, in his article on thermodynamics of the atmosphere in the 'Dictionary of Applied Physics,' vol. iii., gives a computation of the energy of a cycle of operations consisting in the heating of a mass of air at the equator to a sufficiently high potential temperature to enable it to

rise to a height of 15 km. above the equator, after which it drifts northward, losing heat by radiation until it is enabled to descend to the sea-surface in latitude  $60^{\circ}$  N., afterwards returning equatorwards along the earth's surface.

The entropy diagram shows that the amount of energy transformed into work =  $2.4 \cdot 10^{11}$  ergs per kilogramme of air which performs the cycle. Thus the ascent of one kilogramme of air will, if it follows the cycle outlined above, contribute  $2.4 \cdot 10^{11}$  ergs to the energy of the general circulation of the atmosphere. If every second there were  $10^{11}$  kilogrammes of air ascending at the equator, and subsequently following the cycle outlined above, the amount of kinetic energy contributed to the general circulation would just suffice to replace the energy dissipated by turbulence.

This amounts to the ascent of 100 cubic kilometres of air per second, a relatively small quantity by comparison with the size of the equatorial belt along which the propelling power of solar radiation could be exerted.

There is strong evidence of the descent of cold air from the cold slopes of the mountains of Greenland, and of the Antarctic Continent, and the cycle of changes involved in these cases will in the same way yield a contribution to the kinetic energy of the general circulation. L. F. Richardson has estimated that the effect of radiation over the plateau of Greenland is to produce  $10^{20}$  ergs per second, which is but a small fraction of the total dissipation of  $2.5 \cdot 10^{22}$  ergs per second for the whole atmosphere. The descent of air over cold mountain slopes is thus not the most important factor in the maintenance of the circulation of the atmosphere.

The case first considered, of the ascent of air, at the equator raises a fundamental difficulty, in that the thermal stratification of the atmosphere is not favourable to the ascent or descent of air. Further, there is not a direct flow of air from the equator polewards in the upper atmosphere. But in view of the relatively small amount of air which is required to perform the cycle outlined by Sir Napier Shaw, it is only necessary to have a poleward flow of the upper air in a restricted portion of the equatorial belt in order to supply the kinetic energy required. Also the rain of the Dollrum regions affords direct evidence of the ascent of considerable quantities of humid air.

Margules put forward the view that, when cold and warm currents flow side by side, the mixture of the two layers, or the ascent of the warm air over the cold air, releases an amount of energy equal to the decrease in gravitational potential energy. It is, however, easier to conceive of the



process described by Margules giving rise to thunderstorms and linesqualls, than as contributing to the energy of the general circulation. It is not possible to give an estimate of the rate of production of kinetic energy by Margules's process.

It should be noted that all the views here considered visualize the conversion of radiant energy first into potential energy, and the subsequent conversion of the potential energy into kinetic energy.

### 5. Summary.

A rough estimate is given of the total energy of the general circulation of the atmosphere, and an approximate estimate of the rate of dissipation of this energy by turbulence is made, using G. I. Taylor's form of statement of the rate of vertical transference of momentum. It is found that the rate of dissipation of energy is such that, if it were maintained for rather less than a day and no energy were supplied from external sources, it would bring the whole atmosphere to rest; or if the rate of dissipation remained proportional to the total energy, it would reduce the total energy to one-tenth its original value in 3 days. It is further estimated that if about 2 per cent. of the incoming solar radiation were converted into kinetic energy, this amount would suffice to replace the energy taken from the general circulation by turbulence. It is pointed out that no generally acceptable theory has yet been put forward to explain the method of conversion of solar energy into kinetic energy of the general circulation.

**XLIV** *On the Variation of the E.M.F. of a Photoactive Cell, containing a Fluorescent Electrolyte, when the Amount of Fluorescent Material in Solution is Varied.* By WILLIAM RULE, M.Sc., Armstrong College, Newcastle-upon-Tyne\*.

### Introduction.

A NUMBER of experimenters have shown that when one of the electrodes in a cell containing a fluorescent electrolyte is illuminated, the other electrode being kept in the dark, an E.M.F. is set up which varies with time. The most accurate and most recent work on this effect has been

\* Communicated by Prof. G. W. Todd.

done by A. Grumbach\*. He has shown that the E.M.F. developed is greatest and most easily generated in dilute solutions, whereas previous experimenters had used concentrated solutions, and while it had hitherto been contended that the E.M.F. was caused by the illumination of the electrode (the Becquerel effect), he has demonstrated that the phenomenon has not its origin at the surface of the electrode, but that it is essentially bound up with the illumination of the liquid itself.

Plotting E.M.F. against time a curve is obtained, and the present paper contains a description and theoretical discussion of certain experiments carried out to determine the variation of these E.M.F. time-curves when the amount of fluorescent material in solution is varied.

### *Apparatus.*

A number of methods were tried to measure the E.M.F. set up, which is of the order of 50–100 millivolts.

The ordinary bridge method for determining small E.M.F.'s (as in the Crompton Potentiometer) was first used, but was early abandoned: while capable of showing the existence of an E.M.F., the precise measurement of this E.M.F. was impossible as the resistance of the cell was so great that the determining of the null point was very inaccurate. In a second method the cell was connected across a capacity and a charge thrown through a ballistic galvanometer.

$$C \times E = Q \propto \theta \propto \text{Scale reading.}$$

Thus, keeping the capacity constant, the E.M.F. is proportional to the Scale reading and could be determined by suitable calibration. This method was also discarded, as the capacity required to discharge through the galvanometer a quantity of electricity sufficient to give a measurable deflexion was so large as to seriously affect the E.M.F. of the cell; two readings taken the one immediately after the other were found to differ by about 20 per cent. This altering of the conditions of the cell also holds for the bridge method, where the determining of the true E.M.F. of the cell would be rendered impossible by polarization of the cell.

The most satisfactory method proved to be the direct measurement of the E.M.F. on a Dolezalek electrometer, and in all subsequent experiments this instrument has been used.

\* A. Grumbach, *Comptes Rendus*, clxxvi. (January 1923).

Many types of cell were used in the course of trial experiments before a suitable one was evolved. Both mercury and silver were tried as electrodes but proved unsatisfactory, as in each case a discoloration was noticed on the illuminated electrode which was absent from the unilluminated electrode, indicating a photochemical reaction in the neighbourhood of the illuminated electrode.

A serious defect in the cells at first used was the presence of an initial E.M.F. when the cell was set up, due no doubt to the electrodes not being perfectly clean.

This dissymmetrical E.M.F. was, however, reduced to negligible proportions in the cell now to be described, which has been used in the experiments described in this paper. The cell, shown in fig. 1, consists of a glass tube, 20 cm.

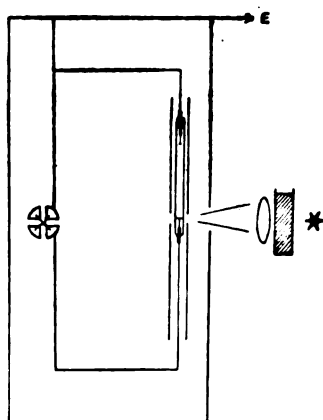
Fig. 1.



long and 2 cm. in diameter, closed at one end, with a platinum wire electrode in the form of a flat spiral fused into the closed end and a rubber stopper, carrying a platinum wire, inserted at the other end. This cell has the advantage that the electrolyte is only in contact with the platinum and the glass, and these can be kept clean by washing out with distilled water and occasionally with chromic and nitric acids and caustic soda.

It is now convenient to describe in detail the whole apparatus shown in fig. 2. Two metal tubes are clamped in an upright position with a gap 1 cm. wide between them. The cell, round which are fixed two guides as shown, is inserted in the metal tubes so that the part of the cell where the flat spiral electrode is situated occupies the gap between the two tubes. This is the electrode which is to be illuminated. Leads are taken from each electrode to the opposite quadrants of the electrometer, the unilluminated electrode and the quadrants to which it is connected being earthed. The needle is charged permanently to 100 volts by means of a hygroscopic battery. On the glass cell, near the electrode which is to be illuminated, is affixed a paper scale,

Fig. 2.



by means of which the cell can be fixed in any desired position within the metal tubes. The whole arrangement is enclosed in an earthed metal box to shield it from external fields. A small aperture in this box allows a beam of light to pass through from outside and fall upon that part of the cell which lies within the gap between the two metal tubes. The illumination is provided by a mercury arc-lamp (240 volts, 2.5 amps.), the full radiation from which is first passed through a water-cell and then concentrated on the surface of the cell by means of a thick lens. With this apparatus the experiments described in the next section were performed.

*Experimental Results.*

As a solution of fluorescein and caustic soda was to be used as an electrolyte, a test experiment was first carried out using a solution of caustic soda in water (0.5 gram NaOH per 100 grams water). It was found that no E.M.F. was set up when caustic soda alone was used in solution. This simple experiment is important in so far as it shows that the E.M.F. set up in the experiments to be described presently is due to the presence of the fluorescent body fluorescein. Also it disproves a contention of Grumbach\* that the action on the electrode of the fluorescent radiation emitted by the illuminated liquid is responsible for part of the E.M.F. generated in a photoactive cell such as we have described. For it is evident that in the cell containing a solution of caustic soda alone, which is much more transparent than a fluorescein solution, and which therefore allows a much more intense and fuller radiation to reach the electrode, there is more likelihood of a photoelectric E.M.F. being set up, whereas in actual fact no observable E.M.F. is generated when a pure caustic soda solution is used. It is thus seen that the essential factor in the building up of an E.M.F. is the activation of the fluorescent material in solution.

The experiments performed with varying concentrations of fluorescent material in solution will now be described.

Special precautions were taken to make up perfectly clean solutions; these were made up in the dark and stored in black flasks, the liquid being kept in the dark until the beginning of an experiment. The cell was thoroughly cleaned out after each experiment in order to prevent there being any appreciable E.M.F. present when the apparatus was set up.

In each experiment the light was concentrated fully on the electrode, which occupied a central position in the cm. gap between the metal tubes.

The concentration of caustic soda was kept constant (0.5 gram per 100 grams of water), while the concentration of fluorescein was varied (from 0.5 gram to 0.00016 gram of fluorescein per 100 c.c. of the caustic soda solution), the most concentrated solution containing about three thousand times as much dissolved fluorescent material as the most dilute solution used.

The variation of E.M.F. with time was then determined for a number of concentrations under identical conditions of illumination and disposition of apparatus. The experiments

\* A. Grumbach, *Comptes Rendus*, clxxvii. (August 1923).

on a series of concentrations were repeated many times with similar results. A typical set of curves is given in figs. 3 and 4.

Fig. 3.

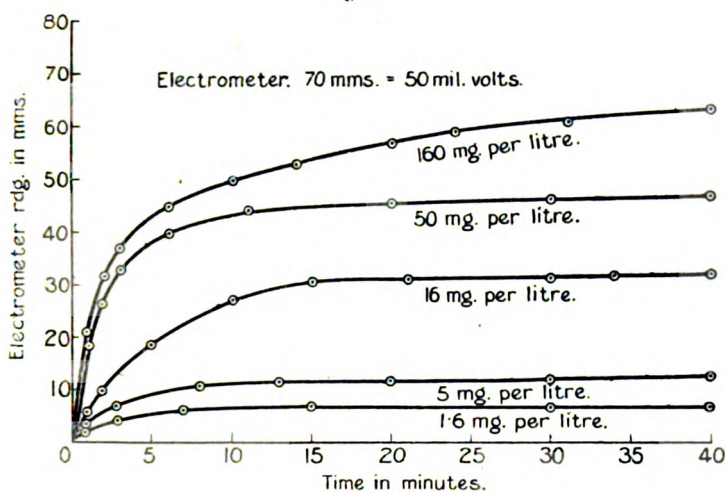
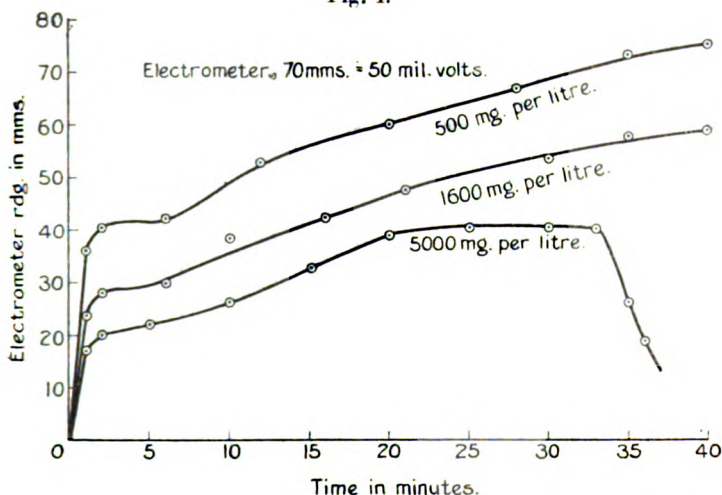


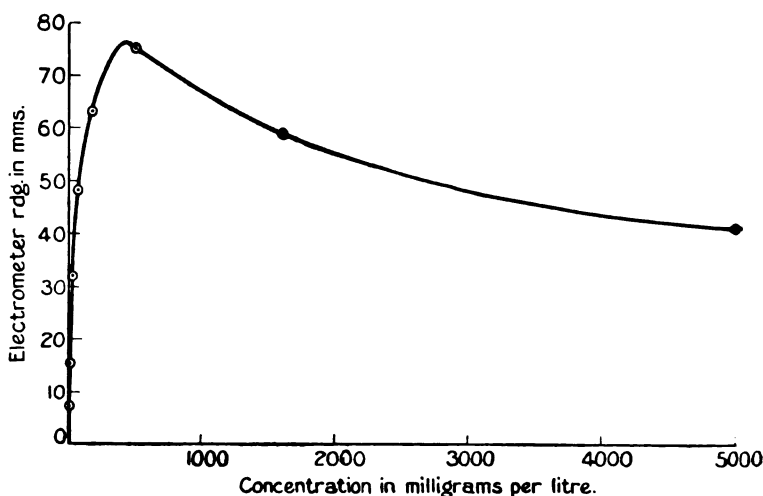
Fig. 4.



It is at once seen that while the form of the curves is similar for various concentrations of fluorescein, the magnitude of the E.M.F. generated in a given time shows a

well-marked variation. Thus for a very concentrated solution the E.M.F. set up is relatively small. As the solution becomes more dilute the E.M.F. generated in a given time increases gradually until it reaches a certain maximum, and then falls rapidly as the dilution is pushed still further. This variation is well shown in the curve given in fig. 5, where the E.M.F. attained in forty minutes (by which time it has in most cases become fairly constant) is plotted against the concentration.

Fig. 5.



The E.M.F. rises quickly to a maximum as the concentration is increased from zero, and then falls off less rapidly as the concentration is increased still further. These experiments have been repeated, using a solution of eosin in glycerine and water (10 gm. of glycerine per 100 gm. of water, and 3.0 to 0.0003 gm. of eosin to 100 c.c. of the glycerine-water solution), and show a variation in the E.M.F. attained in a given time, with concentration, similar to that which holds for fluorescein.

The E.M.F. of the illuminated electrode is negative in the case of the fluorescein solution, while in the case of the eosin solution it is slightly negative at the beginning and then takes up a much larger positive value.

*Analogous Phenomena.*

A.—As an E.M.F. is set up in a photoactive cell when it is illuminated, as previously described, one would expect that if suitable measurements were made a change in conductivity would be observed. Although previous experiments made with this object in view have furnished negative results, Soulan\* has recently shown that this change in conductivity occurs. He gives the following results for esculine dissolved in methyl alcohol :—

N .....	50	20	0.01	0.005,
C .....	0.030	0.035	0.107	0.094,

where N is the number of milligrams of the fluorescent body dissolved per litre of solvent, and C is the limiting relative change in conductivity.

The result is interesting in that it shows the fact that the change in conductivity increases towards a maximum as the concentration decreases, and then falls off as the dilution is pushed still further.

The limiting relative change in conductivity thus varies with concentration in just the same manner as does the E.M.F. with concentration, a result one would have expected.

B.—It is known† that for the production of phosphorescence the essential factor seems to be the bringing into intimate association, in the form of a solid solution, of a small amount of active substance (the solute) and a larger amount of another substance (the solvent). The interesting fact here is that measurements of the intensity of the phosphorescence of solutions of varying concentration have shown that this intensity varies greatly with the amount of active material dissolved; as the concentration increases from zero, the intensity of phosphorescence rises towards a well-defined maximum, and then falls off slightly less rapidly as the amount of active material is still farther increased. This variation is identical with that found to hold for the E.M.F. of a photoactive cell and the concentration.

C.—J. Perrin‡, in a recent paper, refers to the fact that fluorescent solutions are necessarily more fluorescent when they are more concentrated. He gives a curve similar to that given in fig. 5, showing that if the concentration is increased beginning at zero, the fluorescence begins to

\* H. Soulan, *Comptes Rendus*, clxxviii. (March 1924).

† E. Merritt, *Physical Review*, v. (April 1915).

‡ J. Perrin, *Comptes Rendus*, clxxvii. (August 1923).

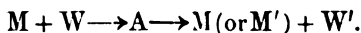


increase, passes through a maximum for an optimum concentration, and then decreases as the concentration is further increased. The intimate association of the E.M.F. set up in an illuminated photoactive cell containing a fluorescent electrolyte with the actual phenomenon of fluorescence is at once seen, and supports the previous contention that the effect which has been the subject of investigation is produced by the photoactivation of the fluorescent material in solution, and that its origin is not at the surface of the electrode.

### *Theoretical.*

It has been shown that the E.M.F. developed in a photoactive cell increases rapidly from zero as the concentration is increased from zero, attains a maximum value for a certain optimum concentration, then falls off less rapidly as the concentration is increased still further. This section is devoted to an explanation of this variation on certain theoretical grounds.

The elementary phenomenon of fluorescence is as follows : A molecule  $M$  of a fluorescent body absorbs a quantum  $W$  of a certain radiation, passes to a critical state  $A$ , from which it returns to the same stable state  $M$  or another stable state  $M'$ , emitting a quantum  $W'$  of another radiation (the fluorescent radiation). Thus :—



Now as the concentration, that is the number of molecules, of the fluorescent body increases from zero, the number of molecules which are activated will also increase. Therefore, assuming that the presence of these molecules in the critical state is responsible in some way for the building up of an E.M.F. in a photoactive cell, as the number of molecules activated increases with increase of concentration, so the E.M.F. will increase with increase of concentration. This explains the first portion of the curve given in fig. 5.

The experiments described, however, show that the E.M.F. does not go on increasing indefinitely, but that it attains a maximum value and then decreases as the concentration is still further increased.

This attaining of a maximum value and subsequent falling off in value of the E.M.F. indicates that, after a certain concentration, the number of molecules in the critical state requisite for the building up of an E.M.F. begins to decrease.

This decrease in the number of molecules in the requisite critical state can be explained if one adopts an hypothesis of

J. Perrin \*, who assumes that in strong concentrations the molecules of the fluorescent body are "protected" by each other.

He explains the mechanism of this "protection" somewhat as follows:—As the concentration increases, the mean distance between the molecules decreases, that is, the molecules are brought into closer proximity to one another. It may be supposed that, if the molecule M, capable of absorbing a quantum of radiation, is thereby brought to a certain critical state A, it takes a certain finite time to attain its new configuration, and that it arrives there by an oscillatory phenomenon. Now if during this time a second molecule of the same nature approaches near the first, it can acquire, by resonance, part of the energy of the first and so disturb its critical state. Thus, as the concentration is increased and the mean distance between the molecules reduced, the "protective" influence of the molecules, the one over the other, increases, and so reduces the number of molecules in the requisite critical state for the building up of an E.M.F. Adopting this hypothesis, the whole of the E.M.F. concentration curve, given in fig. 5, can now be accounted for. When the solution is dilute the "protective" influence of the molecules over each other is small, and so the E.M.F. increases, as the number of activated molecules increases, with increase of concentration. But as the concentration becomes greater, this "protective" influence plays a more and more important part, until the point is reached where the increase in the number of activated molecules due to the mere fact of increase in concentration is compensated for by the reduction in the number of molecules in the requisite critical state, due to the "protective" influence of the molecules over one another. As the concentration is increased still further, the "protective" influence of the molecules over each other brings about a reduction in the number of molecules in the requisite critical state, which is increasingly greater than the increase brought about by the mere fact of the concentration becoming greater.

The maximum point on the E.M.F. concentration curve, and the subsequent falling off in value of the E.M.F. as the concentration is increased, is thus explained.

I wish to acknowledge my indebtedness to Dr. G. W. Todd, of Armstrong College, at whose suggestion and under whose supervision the experiments have been carried out, and to the Department of Scientific and Industrial Research for the grant which has enabled me to undertake the work.

\* J. Perrin, *Comptes Rendus*, clxxviii. (April 1924).

*XLV. Notes on the Superposition of X-Rays and on Scattering. The J Phenomenon (Part III.). By Prof. C. G. BARKLA, F.R.S., and GLADYS I. MACKENZIE, M.A., B.Sc., University of Edinburgh\*.*

ONE of the most remarkable features of the J phenomenon† is the evidence it affords of the divorce of the activity of an X-radiation from the wave-length of that radiation. A complex beam has an activity which is not the sum of the activities of its constituents. Such a beam has properties depending on something analogous to temperature of the radiation as a whole,—properties depending on all its constituents: this much is certain. What it indicates is (under certain conditions at any rate) the separation of quantum relationships from the frequency of radiation. It appears, indeed, that, as far as the J phenomenon is concerned, and possibly much further, there is something more fundamental than frequency; that *something* is measured by absorbability.

An experiment illustrating this and other interesting points in connexion with the scattering of X-rays and with A. H. Compton's hypothesis is briefly described below.

A primary beam is directed from an X-ray tube on to a sheet of radiating substance situated as shown in fig. 1, and the two scattered beams, proceeding in directions making angles of approximately  $60^\circ$  and  $120^\circ$  with the primary beam, are received and measured by the similar electroscopes  $E_2$  and  $E_1$ . Absorbing sheets of the same material and equal thickness are placed at  $F_2$  and  $F_1$  so that the two secondary beams are intercepted in the same way. As the thickness of these absorbing sheets is gradually increased (increased by small steps), we can observe any difference in the absorbability of the radiations by finding the ratio of the ionizations produced in the electroscopes. If the two beams are exactly similar, then similar absorbing sheets should affect them similarly, and the ratio of ionizations should remain constant. Any difference in

\* Communicated by the Authors.

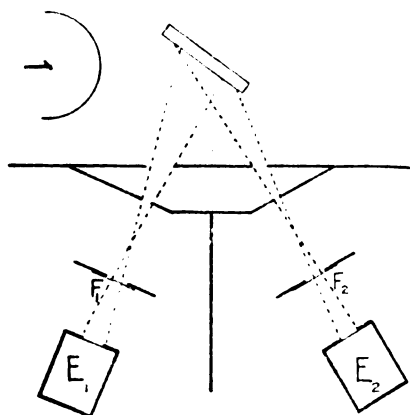
† See "The J Phenomenon in X-Rays" (Part I.), Barkla, *Phil. Mag.* May 1925; (Part II.), Barkla & Khastgir, *Phil. Mag.* Nov. 1925; "The Coherence of Superposed X-Radiations," Barkla & G. Mackenzie, *Nature*, June 20, 1925, and earlier papers referred to.

*Errata:* Part I. For values of  $\left(\frac{\mu}{\rho}\right)_{\text{Cu}}$  in figs. 10 & 11, read 10 times these values; thus, for 1.0 read 10; p. 1037, line 27, for 1921 read 1917; p. 1051, under  $J_1$  Absorption Steps, for  $S=3.5$  read  $\text{Cu}=3.5$ .

constitution of the two beams should show itself by a change in the ratio.

Now according to Compton's hypothesis, if  $\lambda$  be the wave-length of a primary radiation the modified scattered radiation should be of wave-length  $\lambda + \cdot 024(1 - \cos \theta)$ ; hence in the two directions studied the wave-lengths should differ by  $\cdot 024$  Å.U. Over a range of wave-lengths from  $\cdot 6$  Å.U. to  $\cdot 3$  Å.U.—a quite normal range—the difference should vary from 4 per cent. to 8 per cent., and the absorption coefficients should differ by an amount varying from 12 per cent. to 20 per cent. approximately. This is a large difference; one-tenth part of it should be easily measurable.

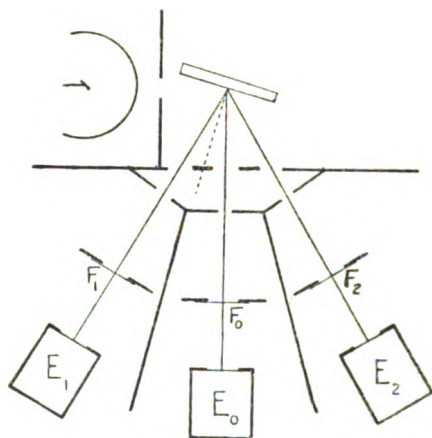
Fig. 1.



It is readily seen that, quite apart from any possible difference of wave-length produced in the two scattered beams proceeding in different directions, unless the primary beam is really homogeneous, a difference in the constitution of the two beams may arise from unequal filtering on emerging from the scattering plate. This, however, is easily eliminated, as in the experiments of Barkla & Ayres on the distribution of scattered radiation, by arranging that the scattered beams studied shall make equal angles with the normal to the scattering plate, and pass through equal thicknesses of that plate. This has been arranged in the later experiments. But even this precaution is unnecessary if either a very thin or a very thick sheet of scattering substance is used. It is unnecessary, too, in a substance consisting of very light atoms, for in this there is very little

selection of constituent radiations, the absorption of the different constituents varying very little with wave-length of the radiation: such a substance is paraffin wax. Consequently, in these earlier experiments with paraffin wax, and even with aluminium as scattering substances, there was little effect of difference of obliquity of the two scattered beams; and what there was would tend to increase the difference of absorbability as expected in these two directions on A. H. Compton's hypothesis. It was in order to make the conditions as simple as possible, and to remove all possibility of the effect of unknown quantities, that we more recently arranged that the two directions of the scattered radiations tested should make the same angle with the normal, and so pass through equal thicknesses of absorbing substances, as do the beams entering electroscopes  $E_0$  and  $E_1$

Fig 2.



in fig. 2. The results of the two sets of experiments are identical in nature.

We obtained such an interesting series of results with the arrangement of fig. 1, that we give an account of them below. Fig. 3 shows the results of fifteen consecutive series of experiments. In each series the ratio of ionizations  $I_1/I_2$  produced in the two electroscopes  $E_1$  and  $E_2$  was obtained when no intercepting sheet was placed in their path; then the ratio of ionizations for equal and increasing thicknesses of aluminium placed in the two beams. In fig. 3 the ratio of ionizations  $I_1/I_2$  is plotted against thickness of

absorbing aluminium. The remarkable features shown are the following :—

(1) In all the long series of fifteen experiments, fourteen

Fig. 3.

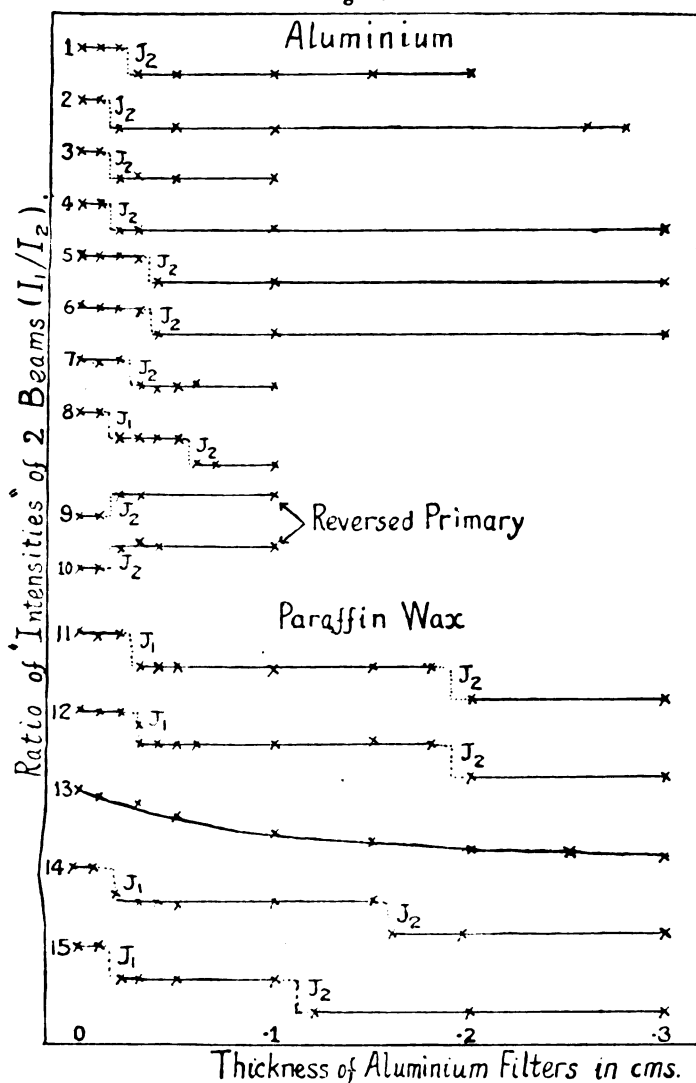


exhibit no difference between the two scattered beams except at the  $J$  discontinuities ; this is shown by the horizontality of the lines indicating that one beam is absorbed exactly

as the other. In some of these experiments as much as about 75 per cent. of the total ionization was cut off between the discontinuities, so that the test of equality of penetrating power was a very sensitive one. A 2 per cent. difference of absorption coefficient would have been easily observed. Compton's "modified radiation" would give a 15 per cent. to 20 per cent. difference; if such a modified radiation had been present it could not have been more than 10 per cent. (probably much less) of the whole scattered radiation. There is no evidence of its existence at all.

(2) In all these experiments, however (all excepting Experiment 13), the J discontinuities were shown by *one* scattered beam but not by the other. The beam showing the discontinuities was the beam at an angle of  $120^\circ$  with the primary, for this beam exhibited a sudden *diminution* of intensity relative to the other. That is, the beam proceeding somewhat backward upon the primary showed at certain critical thicknesses of filtering aluminium the sudden diminution of intensity; the scattered beam proceeding somewhat forward did not show this. This was confirmed by simultaneous measurements in three directions. When the direction of the primary was reversed, *i. e.* the X-ray tube was placed on the other side of the scattering plate while everything else was unchanged, then the other electroscopes  $E_2$  showed the discontinuity, for the ratio  $I_1/I_2$  as previously measured suddenly *rose* at the J discontinuity (see Experiments 9 & 10, fig. 3). This experiment showed that the occurrence of the discontinuity in the beam at an angle of  $120^\circ$  with the primary was not due to any peculiarity of situation or configuration, except with regard to the primary radiation.

In the whole series of experiments, with the exception of No. 13, not a single J discontinuity was missed.

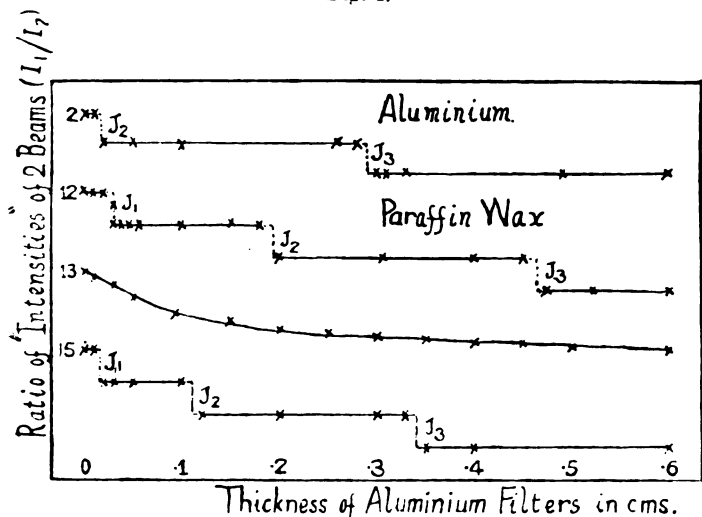
The values of the absorption coefficient ( $\frac{\mu}{\rho}$  in Al) calculated from a 50 per cent. "absorption" of the beam which gave the discontinuity, agreed remarkably well with those previously obtained for beams of various kinds. Thus the values for the  $J_1$ ,  $J_2$ , and  $J_3$  discontinuities respectively were:—

$J_1$ .....	3.4, 3.6, 3.6, 3.7, 3.6,	average 3.6.
$J_2$ .....	1.85, 1.9, 2, 2.1, 2.1, 1.95, 1.9, 2, 2, 1.9, 2, 2, 2,	average 2.
$J_3$ .....	.71, .75, .8,	average .75.

as compared with 3.8, 1.9, and 0.7 previously published.

The three discontinuities were, however, in our experiments obtained by filtering one complex radiation, the three discontinuities appearing one after the other in the appropriate positions. The results of these more extensive series of filtering experiments are shown in fig. 4.

Fig. 4.



The magnitude of the discontinuities in the absorption of the radiations scattered from aluminium was exhibited by a sudden drop of about 7.5 per cent. in the ionization produced in the electroscope; when paraffin wax was used as scattering substance the magnitude was about 10 per cent.

Thus, although the two beams from paraffin wax, for instance, were normally absorbed at the same rate (see Experiments 11, 12, 14, 15 in fig. 3), the beam making an angle of  $120^\circ$  with the primary showed these three sudden

falls in ionizing power when the values of  $\frac{\mu}{\rho}$  (calculated from a 50 per cent. absorption, or rather 50 per cent. diminution in ionization) were 3.6, 2.0, and 0.75, and the whole beam had its ionizing action cut down by about 27 per cent. relative to the beam scattered at  $60^\circ$ . (It seems probable that if the filtering could have been carried further, the  $J_4$  and  $J_5$  discontinuities would also have occurred; and there is no reason to think that even the  $J_5$  discontinuity is



the last)\*. Thus, though between these J discontinuities the absorption coefficients of the two scattered radiations are identical, there is some quality of the radiation which causes the intensity of one radiation during transmission to fall abruptly when certain average penetrating powers are reached. We, of course, usually attribute such a drop in intensity, as measured in an electroscope, to an increase in absorption in the substance traversed. That this is so is evident from the fact that the aluminium or other absorbing substance does emit an increased electronic radiation—there is a true absorption of energy†.

When the primary beam was “softened,” the filtering had to proceed a little further before the critical absorbability was reached; when “hardened” the discontinuity occurred earlier in the filtering process. This is seen by a comparison of the positions of the discontinuities in fig. 3 with the corresponding absorption coefficients of the *unintercepted* beams given in Column 4 of Table I., in which the results are collected. The position of the discontinuities was thus under control, as will be further demonstrated below.

Now it is perfectly evident that the sudden absorption occurring in a heterogeneous beam as it is filtered is not due to the appearance of any particular wave-length in the filtered radiation. On the other hand, these sudden increases in the absorption occur so persistently at very definite absorption coefficients, though this appears to be only an average absorption coefficient, that we are driven (not by these experiments alone, but by scores of experiments illustrating the same feature) to the conclusion that this so-called absorption coefficient indicates something much more fundamental than has hitherto appeared. For some years we were unprepared to accept the conclusion; it appeared to have no very definite physical significance. In many ways, however, wave-length is shown to be totally irrelevant except by its association with a certain absorption.

As we have pointed out previously in this connexion, temperature is likewise only an average, and the properties of substances depend, not on the energies of individual molecules, but on the average energy.

The sudden disappearance of energy from the beam of X-rays and appearance of energy in electrons of the transmitted substance indicates a concentration of the energy of

\* This experiment shows how the dissymmetry of the scattered radiation on the two sides of the plane normal to the direction of primary propagation develops.

† See Bakerian Lecture, 1916 (Phil. Trans. 1917); other results unpublished.

the beam in certain atoms of the substance traversed, or whatever view we hold regarding radiation, it is a change of state of the energy of radiation. But certain conditions are necessary for the concentration of energy, as certain nuclei are essential to the condensation of a vapour. What under some conditions takes place continuously, under other conditions occurs discontinuously. This is well illustrated

TABLE I.

Number of Experiment.	Scattering Substance.	Thickness of Scatterer.	"Absorption Coefficients" of Unintercepted Radiations	"Absorption Coefficients" at J Discontinuities.		
				$\left(\frac{\mu}{\rho}\right)_{\Delta 1}$	$\left(\frac{\mu}{\rho}\right)_{\Delta 1} J_1$	$\left(\frac{\mu}{\rho}\right)_{\Delta 1} J_2$
1 .....	Aluminium	1.9 cm.	2.8	...	1.85	
2 .....	"	"	2.5	...	1.9	.71
3 .....	"	"	2.5	...	2	
4 .....	"	"	2.6	...	2.1	
5 .....	"	.6 cm.	3.4	...	2.1	
6 .....	"	.3 cm.	3.5	...	2.1	
7 .....	"	1.9 cm.	3.0	...	1.95	
8 .....	"	.3 cm.	4.0	3.6	1.9	
9 .....	"	"	2.6	...	2	
10 .....	"	"	2.6	...	2	
11 .....	Paraffin Wax	1.7 cm.	4.3	3.6	1.9	
12 .....	"	"	4.5	3.6	2	.75
13 .....	"	"	4.4			
14 .....	"	"	4.3	3.7	2	
15 .....	"	.7 cm.	4.6	3.6	2	.8

by the results of Experiment 13 and other experiments, in which the difference between the two secondary beams is shown by the *continuously* greater absorption of the beam at  $120^\circ$ ; this is indicated by a continuous curve sloping down to the right. What in Experiment 13 takes place continuously, in other experiments takes place in jumps, and these jumps occur at definite absorbabilities. But the strange feature is that we are not yet able to recognize any difference between Experiment 13 and Experiments 12 and 14 except in the result. Clearly in *all* of these experiments there is a difference between the two scattered beams, but

in one case it remains latent until these critical absorbabilities are reached.

It should be added that we have more recently obtained series of consecutive experimental results of both kinds—those showing a difference between the two beams by discontinuities and those showing a difference continuously\*.

In a discussion of the theory of X-ray scattering, two cases (*a*) and (*b*) have thus again to be considered, as in the comparison of the radiation scattered at  $90^\circ$  with the primary radiation (Phil. Mag. Nov. 1925).

In *Case a* the difference between the scattered beams is shown only by discontinuities in the absorption of the radiation scattered at  $120^\circ$ ; otherwise no difference appears. In this case there is definitely no difference of wave-length if, as is usually assumed, the absorbability and general activity of an X-radiation depend only upon wave-length or frequency. But we have shown that a change of absorption and the associated phenomena do occur without a change of wave-length. Can a change in wave-length occur without a change in absorbability, etc.? Our results classified as *Case a* are only reconcilable with a change of wave-length if the activity of an X-radiation depends fundamentally on something other than waves, for we certainly do not get the change of properties which normally accompany a change of wave-length.

In *Case b*, illustrated by Experiment 13, in which the two scattered beams differ in absorbability, there might be a difference of wave-length between the two scattered beams, if further experiments did not indicate otherwise. But as we have found that a similar difference of absorbability sometimes appears between the scattered and the primary radiation—a difference which cannot depend primarily upon a change of wave-length, for it is shown in some substances when not in others,—we must conclude that the difference appearing in these experiments between the two scattered beams is not due to a difference in wave-length.

The plain fact is, that having shown the detachment of X-ray phenomena from mere frequency, it seems just possible that diffraction methods indicate a change of wave-length, whereas our methods indicate no corresponding change of properties, because those properties are not fundamentally and inseparably associated with waves. But it is not our intention in this paper to explore the whole range of

\* In addition to those showing no difference whatever between the two scattered beams.

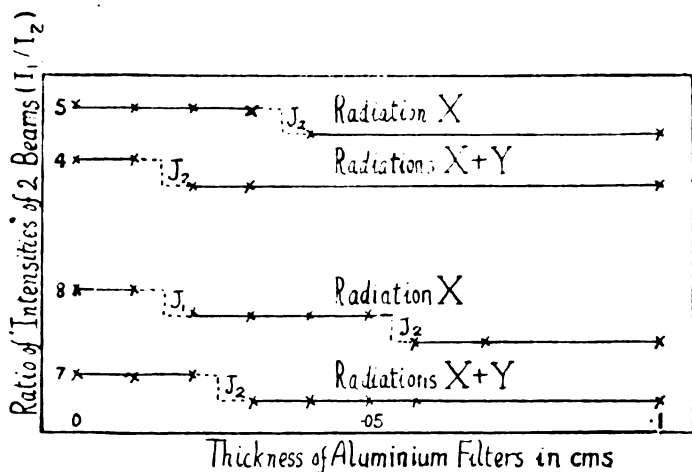
possibilities, logical and illogical: further experiments alone will enable us to solve these fundamental problems.

For the present we can say that if measured by the general activity (as distinct from the activity in particular substances) there is no difference of wave-length between the two radiations.

*Superposition of Two Beams of X-rays.*

That the J absorption and all the associated phenomena depend on the whole of a complex beam, and not on any of its components or even any group of its components, is shown most directly by the following experiments. A thin sheet of scattering aluminium was placed in position as before, and the thickness of filtering aluminium at which the J discontinuity occurred was found. When a thicker sheet of scattering substance was placed behind the first so that

FIG. 5.



there was superposed on the radiation previously experimented upon a more penetrating radiation from deeper layers, it was found that the first discontinuity had disappeared, but that in its place, that is at a thickness of filtering aluminium appropriate to the complex beam as a whole, there appeared the full discontinuity.

Thus Experiment 5, fig. 5, was made with a scattering sheet of aluminium .6 cm. in thickness, and showed the J discontinuity at a thickness of filtering aluminium between .03 and .04 cm., whereas when the thickness of scattering

## 552 *On the Superposition of X-Rays and on Scattering.*

aluminium was increased to 1.9 cm. and the ionization in the electroscope was (roughly) doubled, the  $J_2$  discontinuity occurred for a thickness of filtering aluminium between the .01 and .02 cm. (Experiment 4, fig. 5). In order to avoid any possible effect due to a change in the primary radiation, the readings with the two thicknesses of scattering substance were taken in alternate pairs, so that corresponding points were obtained with practically identical radiations. A similar method was adopted in Experiments 8 and 7. It may be noticed that in Experiment 8 (fig. 5), with the thin sheet only .3 cm. in thickness, the scattered beam was sufficiently soft to show the  $J_1$  discontinuity in addition to  $J_2$ . With the additional thickness of 1.6 cm. of scattering aluminium, making a total thickness of 1.9 cm. (that is, in Experiment 7), the  $J_1$  discontinuity was driven out of the range of experiments, and the  $J_2$  discontinuity was displaced from a thickness between .05 and .06 cm. to between .02 and .03 cm. No more direct experiment could be devised to show the coherence of constituent radiations. By this we mean that the  $J$  phenomenon is independent of individual harmonic constituents of a radiation, but dependent on the combination.

It is important to determine what conditions are necessary for the coherence of a complex beam. Must the two constituent beams be excited by the same primary beam, and must they be excited in the same substance? This point is at present under investigation, but it may be said that in preliminary experiments, when the first layers were of paraffin wax and the deeper layers of aluminium, there certainly was not the simple coalescence described above.

In addition, we have had scattered radiations excited by the same primary beam from air and from paper proceeding at the same time into the same electroscope in practically the same direction. The radiation from air was like the primary, that from paper was unlike. Thus these two beams appeared entirely independent.

### *Summary.*

Three  $J$  discontinuities,  $J_1$ ,  $J_2$ , and  $J_3$ , have been obtained in the absorption of one complex beam of X-rays by placing a gradually increasing thickness of aluminium in the path of the beam. (These were originally discovered by a quite different method and with different radiations— $J_1$  with scattered X-rays,  $J_2$  with characteristic rays of the K series,  $J_3$  with primary rays.)

It has also been shown by the superposition of two scattered radiations that the activity of the compound radiation is not the sum of the activities of the two constituent radiations. Further than that, each beam, as far as the J phenomenon is concerned, acts as a whole, and the compound beam, consisting of the two, behaves as a radiation of intermediate absorbability, showing not two discontinuities for the constituent beams, but one appropriate to the beam as a whole.

The activity of a radiation thus depends, in part at least, on something analogous to temperature of the radiation as a whole. This shows the separation of the activity of X-rays from the frequency or wave-length of the radiation, and illustrates the coherence of constituent radiation. It suggests the separation of quantum actions from the frequency with which they have always been associated.

Two beams of X-rays scattered in directions making angles  $60^\circ$  and  $120^\circ$  with the primary radiation differ, when at all, in one of two ways—(a) by the beam at  $120^\circ$  showing the J discontinuities, the other not (otherwise there is no difference of absorbability); or (b) by a continuous difference of absorbability in *some* substances. Neither of these can be reconciled with a true difference of wave-length, unless a change of wave-length can occur without the usual accompanying change in absorbability and general properties in *all* substances.

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XLVI. *Properties of the Generalized Artificial Line.*

By The Research Staff of the General Electric Co., Ltd.\*

(Work conducted by A. C. BARTLETT.)

SUMMARY.

It is shown that there exists a "Bridge" type artificial line section equivalent to the generalized artificial line section, and that results similar to those given previously for the  $\Pi$  and T section line (Phil. Mag. April 1925) hold for the generalized artificial line.

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THE theory has already been given† of a generalized artificial line constructed of sections such as fig. 1, where each section is symmetrical about a centre element  $x_n$  which will be either shunt or series according as  $n$  is even or odd.

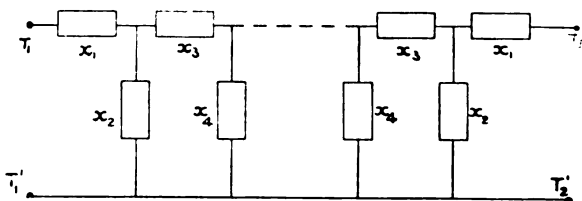
\* Communicated by the Director.

† Phil. Mag. xxxix. p. 1072 (May 1925).

It was shown that, if the impedances of  $x_1, x_3$ , etc. are  $a_1, a_3$ , etc., and the impedances of  $x_2, x_4$  are  $\frac{1}{a_2}, \frac{1}{a_4}$ , etc., the line characteristic impedance of the artificial line is given by

$$\sqrt{\frac{K(a_1, a_2 \dots, a_n \dots, a_2, a_1)}{K(a_2, a_3 \dots, a_n \dots, a_3, a_2)}}.$$

Fig. 1.



A property of continuants is that

$$\begin{aligned} K(a_1, a_2 \dots, a_n, \dots, a_2, a_1) \\ = 2K(a_1, a_2 \dots, a_{n-1} K(a_1, a_2 \dots, a_{n-1}, \frac{a_n}{2})), \end{aligned}$$

and applying this to both numerator and denominator,

$$Z_0 = \sqrt{\frac{K(a_1, a_2 \dots a_{n-1}) K(a_1, a_2 \dots, a_{n-1}, \frac{a_n}{2})}{K(a_2, a_3 \dots a_{n-1}) K(a_2, a_3 \dots, a_{n-1}, \frac{a_n}{2})}},$$

which is of the form :

$$Z_0 = \sqrt{P \times Q},$$

where

$$P = \frac{K(a_1, a_2 \dots, a_{n-1})}{K(a_2, a_3 \dots, a_{n-1})},$$

$$Q = \frac{K(a_1, a_2 \dots, a_{n-1}, \frac{a_n}{2})}{K(a_2, a_3 \dots, a_{n-1}, \frac{a_n}{2})}.$$

P and Q are obviously impedances ; P is the impedance of the network of fig. 2 (a) if  $n$  is even, and of fig. 2 (b) if  $n$  is odd ; Q is the impedance of the network of fig. 3 (a) if  $n$  is even, and of fig. 3 (b) if  $n$  is odd.

Fig. 2.

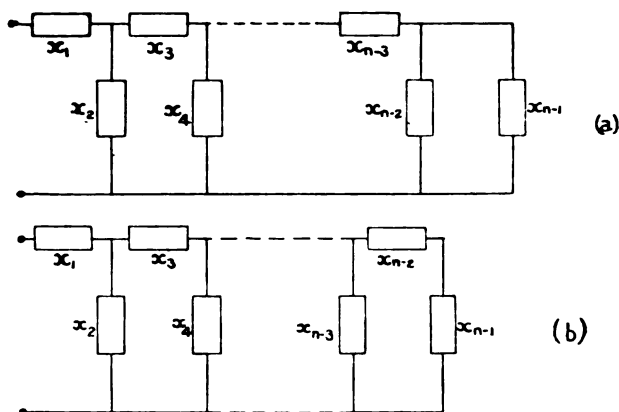
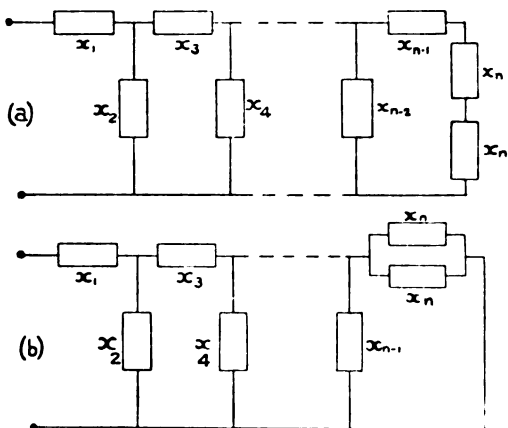


Fig. 3



A bridge section having arms P and Q will thus have the same line characteristic impedance as the original section. If its propagation constant is  $\phi$ ,

$$Z_0 \tanh \phi = \frac{2}{\frac{1}{Z_0 \coth \frac{\phi}{2}} + \frac{1}{Z_0 \tanh \frac{\phi}{2}}} \\ = \frac{2}{1/P + 1/Q}.$$



On inserting values of  $P$  and  $Q$  this is found to be equal to

$$\frac{K(a_1, \dots, a_n, \dots, a_1)}{K(a_2, \dots, a_n, \dots, a_1)},$$

which is  $Z_0 \tanh \theta$  where  $\theta$  is the propagation constant of the original line.

Thus the bridge section with arms  $P$  and  $Q$  has the same line characteristic impedance and the same propagation constant as the original section, and is identically equivalent to it.  $P$  and  $Q$  must therefore have the values

$$Z_0 \tanh \frac{\theta}{2} \quad \text{and} \quad Z_0 \coth \frac{\theta}{2}$$

but it has still to be determined which is the value of  $P$  and which is the value of  $Q$ ; that is to say, there is an uncertainty which of the output terminals of the bridge section correspond to which of the original section.

The receiving end impedance of one section of the original artificial line short-circuited at the far end is  $Z_0 \sinh \theta$ , which from first principles is

$$K(a_1 \dots a_n, \dots, a_1).$$

Assuming, first, that

$$P = Z_0 \coth \frac{\theta}{2} \quad \text{and} \quad Q = Z_0 \tanh \frac{\theta}{2};$$

then

$$\begin{aligned} Z_0 \sinh \theta &= \frac{1}{\frac{2}{Z_0 \tanh \frac{\theta}{2}} - \frac{2}{Z_0 \coth \frac{\theta}{2}}} \\ &= \frac{1}{2} \cdot \frac{1}{\frac{1}{Z_0 \tanh \frac{\theta}{2}} - \frac{1}{Z_0 \coth \frac{\theta}{2}}} \\ &= (-1)^{n-1} K(a_1, \dots, a_n, \dots, a_1). \end{aligned}$$

This is equal to the value previously obtained only if  $n$  is odd. Hence, when  $n$  is odd,

$$P = Z_0 \coth \frac{\theta}{2},$$

$$Q = Z_0 \tanh \frac{\theta}{2};$$

and similarly when  $n$  is even

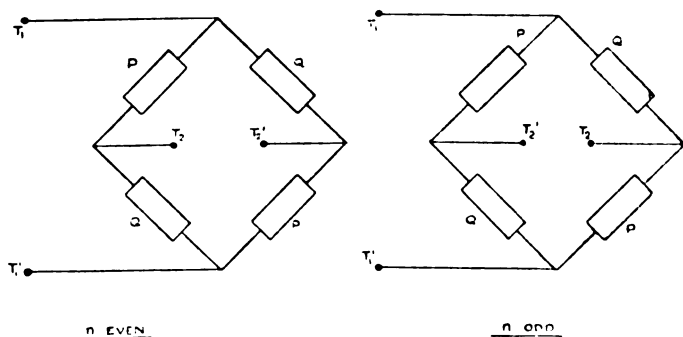
$$P = Z_0 \tanh \frac{\theta}{2},$$

$$Q = Z_0 \coth \frac{\theta}{2}.$$

Thus the correspondence of the terminals is as shown in fig. 4.

The original section can be cut exactly into halves by replacing the central impedance by two impedances of half its value in series if  $n$  is odd, or by two impedances of double its value in parallel if  $n$  is even. It is interesting to note

Fig. 4.



that, whether  $n$  is odd or even,  $Z_0 \coth \frac{\theta}{2}$  is then the impedance of a half section open circuited at the far end and  $Z_0 \tanh \frac{\theta}{2}$  is the impedance of a half section short-circuited at the far end.

It is further seen that, since the impedances  $Z \coth \theta$ ,  $Z_0 \tanh \theta$ ,  $Z_0 \coth \frac{\theta}{2}$ ,  $Z_0 \tanh \frac{\theta}{2}$  can be constructed, the results previously given\* for the simple  $\Pi$  and  $T$  sections also hold for the generalized artificial line.

Thus there exist a number of alternative networks that have the same impedance as an artificial line made up of any number of sections short-, or open-circuited at the far end or terminated by  $Z \tanh \frac{\theta}{2}$  or  $Z_0 \coth \frac{\theta}{2}$ . Further, a single bridge type section can be constructed in a number of ways so as to be equivalent both as regards input and output terminals to an artificial line consisting of any number of sections.

\* Phil. Mag. xlix. p. 728 (April 1925).

# XLVII. *Proceedings of Learned Societies.*

## GEOLOGICAL SOCIETY.

[Continued from ser. 6, vol. 50, p. 1298.]

May 6th. 1925.—Dr. J. W. Evans, C.B.E., F.R.S.,  
President, in the Chair.

Mr. EDWARD BATTERSBY BAILEY, M.C., B.A., F.R.S.E., F.G.S., delivered a lecture on the Tertiary Igneous Geology of the Island of Mull, illustrated by lantern-slides.

He asked his hearers to remember that he was only one of a small group of workers who had recently been employed in adding to our knowledge of the geology of Mull. In the Geological Survey Memoir (1924), the share of each participant is indicated by initials.

The columnar lavas of Staffa and South-Western Mull were described, with especial reference to Scrope's double-tier jointing. Iddings's explanation of the apparent repugnance of approaching columns, and Macculloch's tree that stands upright although submerged in lava.

Attention was then focussed upon Judd's region of central pneumatolysis (propylitization), where, within an area measuring 15 miles in diameter, it is impossible to find a lava that has retained its olivine undecomposed.

Judd's conception of central subsidence was next discussed. It now appears, from the disposition of lava-types and other considerations, that central subsidence culminates in two adjacent calderas. The occurrence of many pillow-lavas within one of these calderas—at the centre of a manifestly terrestrial volcano—points to the frequent presence of a crater-lake. The crater-hollow must have been renewed by intermittent subsidence—for instance, Kilauea and Askja. The rim-craters of Askja may be taken as a surface-manifestation of a ring-dyke. Ring-dykes are numerous in Mull, where their most perfect example is the Loch Ba felsite, traced by Mr. W. B. Wright and Mr. J. E. Richey. Ring-dykes are known at other British Tertiary centres, and also at Glen Coe and Ben Nevis. Many ring-structures occur in Iceland, in addition to the Askja caldera, and have been described by Thoroddsen. At Oslo they appear in Brøgger & Schetelig's map (1923).

There is conspicuous folding in Mull attributable to the lateral expansion of an early ring-dyke. Similar folding does not recur in connexion with later ring-dykes. These may, in some cases, have made room for themselves by stoping en masse, and in others by pushing country-rock inwards towards a central orifice.

Several ring-dykes in Mull show gravitational differentiation, and the lecturer explained that he had been convinced by Dr. H. H. Thomas and Mr. A. F. Hallimond that this had taken place during crystallization.

Cone-sheets were passed in review, and emphasis laid on their great aggregate bulk.

Finally, the Mull swarm of north-westerly dykes was considered. The dyke-swarm owes its location to the previous development of the central conduit. One of its members, with ash-vents distributed along its course, has furnished Dr. B. N. Peach and others with a convincing analogue of the Laki fissure in Iceland. Probably, many of the Mull dykes fed fissure-eruptions, as Sir Archibald Geikie long ago maintained; but the products of most, if not all, of these eruptions have been eroded away.

June 16th.,—Dr. J. W. Evans, C.B.E., F.R.S., President,  
in the Chair.

The following communication was read:—

‘On some Occurrences of Spherulitic Siderite and other Carbonates in Sediments’. By Edmondson Spencer, B.Sc., Ph.D., F.G.S.

The author gives descriptions of a number of spherulitic aggregates (many of which have been described as oolitic) in freshwater clays and in coals. The occurrences, which are considered in detail, include those in the Fairlight Beds, the Upper Coal Measures of Staffordshire and South Wales, the Upper Wankie Sandstone Series (Rhodesia), and the coals of the Damuda Basin (India). For comparison with these, spherulites with radiolaria from Santo Domingo (Portugal) are described.

The spherulites are composed of rhombohedral carbonates, usually siderite, but occasionally of calcite, sideroplesite, dolomite, or a mixture of manganese and iron carbonates (as at Santo Domingo). By treating thin slides of the spherulitic siderite (after heating to redness) with warm hydrochloric acid and stannous chloride, the iron is removed and the structure, as outlined by occluded sedimentary material (such as clay or coal), may be studied.

Certain common characters are observed: (1) The spherulites occur in association with fine-grained sediments of carbonaceous,

muddy, or silty type, often with comminuted plant-tissue; (2) the deposits seem, without exception, to be of freshwater origin and devoid of calcareous shelly remains; (3) the carbonate material in most cases consists of nearly pure siderite, with a little carbonate of magnesium and calcium (usually in dolomite-proportions); (4) the spherulites are fairly uniform in size locally: the smallest series has a diameter of about 0.5 mm. and the largest series 2 to 3 mm.; (5) the occluded sediment is similar to that in which the spherulites are embedded, and has been enclosed during their growth; and (6) where 'zoning' of the sediment occurs, it is subordinate to radial structure.

It is concluded that the spherulites have formed from iron-carbonate solutions held within the gradually settling and consolidating sediment. The contrast in the character of carbonate chemically precipitated from solution (as in the blackband and clay-ironstones) is noted.

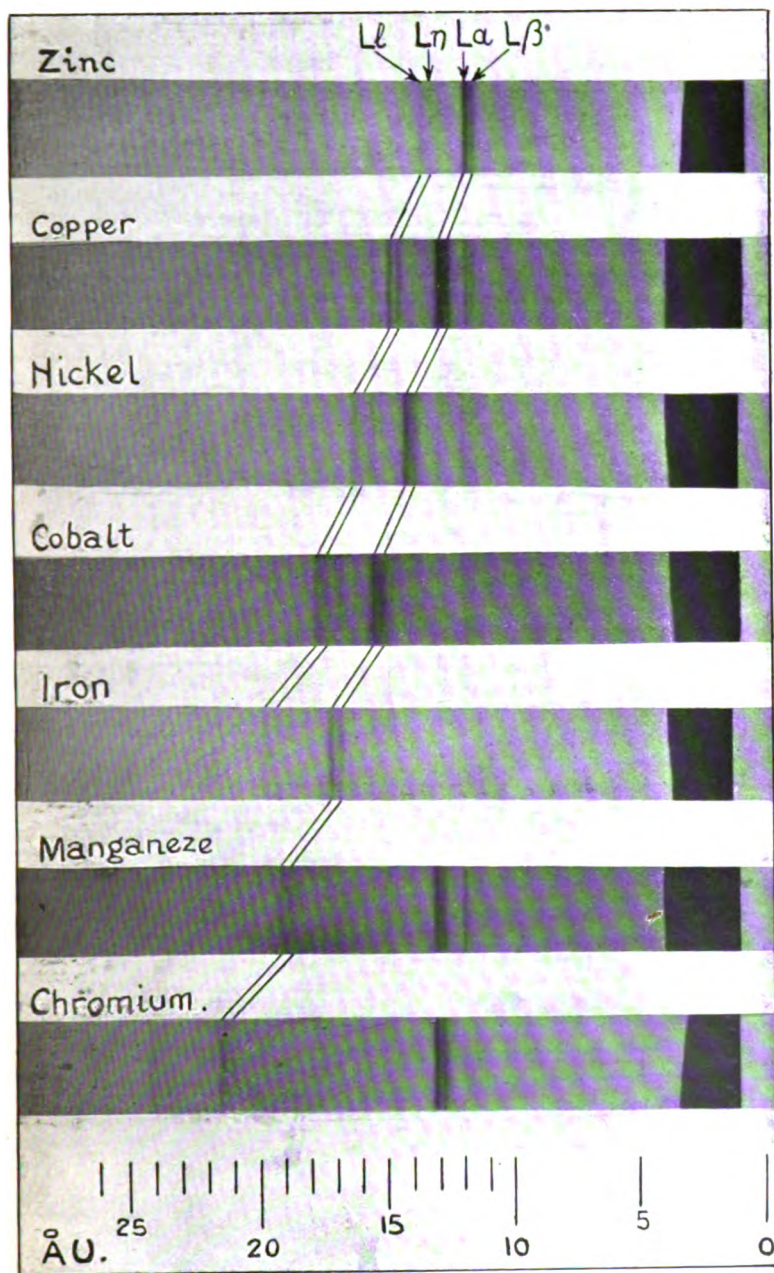
The reactions resulting from the presence in sediments of humate compounds, salt, calcium carbonate, etc. are considered. The author believes that the iron compounds present in solution in fresh water as carbonates, humates, or hydrolized and possibly colloidal hydrates, were adsorbed by the fine-grained and partly colloidal sediments, and were carried down with them during deposition. Conditions of supersaturation would result from the settling and flocculation of the sediment, and from the gradual upward expulsion of the more readily diffused water-molecules. Crystallization would then commence at a number of centres simultaneously, the spherulitic growth ceasing before the consolidation of the sediment was completed. Comparisons are instituted with well-known diffusion phenomena in colloidal media resulting in the production of 'zoning'.

Interfering surfaces between adjoining spherulites are mostly plane, but occasionally are slightly concave to the smaller individuals.

In an Appendix, the author discusses mathematically the form of the surface of contact between spherulites, as determined by various rates of growth.

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[The Editors do not hold themselves responsible for the views expressed by their correspondents.]





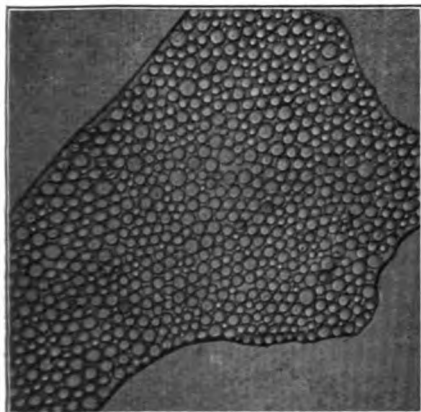


FIG. 1.

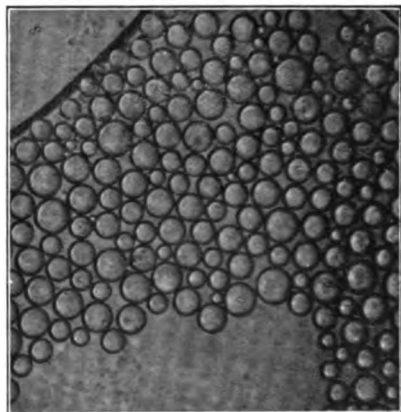


FIG. 2.

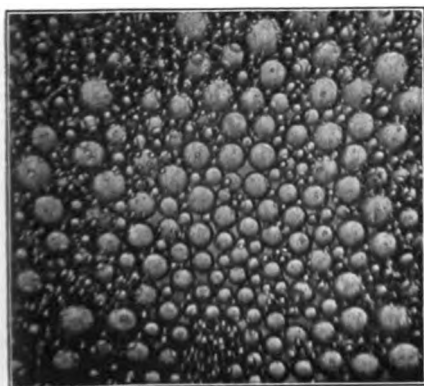


FIG. 3.



FIG. 4.

**Chromatic Emulsions.**





FIG. 2.

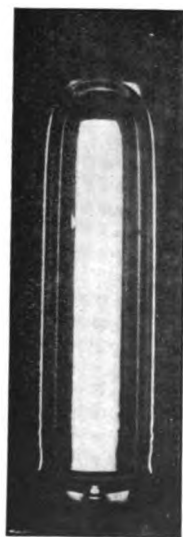
A.



B.



D.



C.

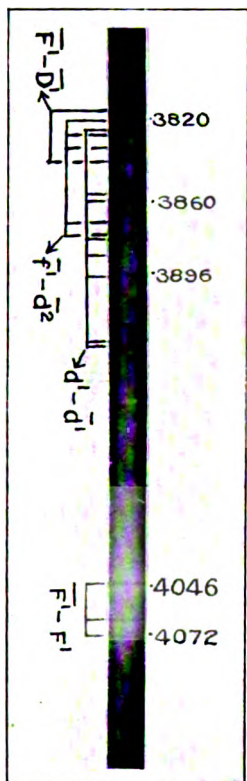
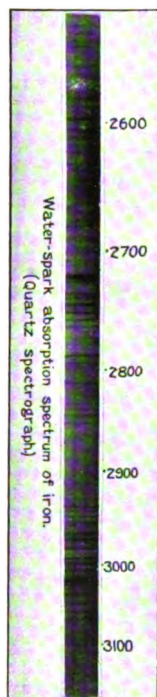


A & B. Machine Oil in tube 0.646 cm. diam.  
(The tube was differently masked to define outline  
of the bubble.)

C. Water in tube 0.646 cm. diam.

D. Water in tube 1.0 cm. diam.







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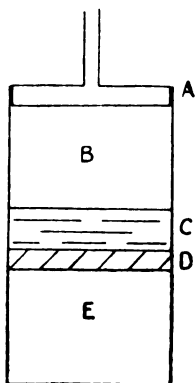
MARCH 1926.

XLVIII. *The Effect of the Presence of an "Indifferent" Gas on the Concentration and Activity of a Vapour in Equilibrium with a Condensed Phase or System of Condensed Phases.* By IVAN ROY MCHAFFIE\*.

*Introductory.*

THE effect of the presence of an indifferent gas on the concentration and activity of a vapour in equilibrium with a condensed (solid or liquid) phase may be expressed quantitatively in the following manner. The concentration of the indifferent gas may be increased by increasing its

Fig. 1.



pressure in a vapour chamber in contact with the condensed phase according to the system shown in fig. 1. A represents a piston exerting a pressure  $P$ ; B a chamber containing the

\* Communicated by Prof. F. G. Donnan, F.R.S.

*Phil. Mag.* S. 7. Vol. 1. No. 3. March 1926.

2 C



indifferent gas and vapour from C; C the solid (or liquid) system; D a fixed semipermeable membrane permeable only to the vapour of C; E a chamber containing only this vapour. It is assumed that, at the chosen temperature T, the pressure of vapour in E is small. It will also be small in B. It is also assumed that the effect of the solubility of the indifferent gas in C may be neglected, and that C is a pure solid (or liquid) substance S.

If  $F_s$  be the molar free energy\* of the solid (or liquid) S at the temperature T and the pressure P;  $F$  the corresponding molar free energy of S vapour in E; and  $\bar{F}$  the partial molar free energy of S vapour in B, then, when equilibrium is reached,

$$\bar{F} = F_s = F.$$

For a change in total pressure, the temperature remaining constant,

$$\left(\frac{\partial \bar{F}}{\partial P}\right)_T = \left(\frac{\partial F}{\partial P}\right)_T = \left(\frac{\partial F_s}{\partial P}\right)_T = V_s, \dots (1)$$

where  $V_s$  is the molar volume of the solid (or liquid) substance S. It is supposed in the present case that the increase of pressure is caused by an increase in the concentration (and partial pressure) of the indifferent gas.

Let  $F_0$  be the molar free energy of S vapour in some standard state. If in all states S vapour follows ideal gas behaviour, then, for an isothermal process,

$$\bar{F} - F_0 = RT \log \frac{c}{c_0},$$

where  $c$  and  $c_0$  are the concentrations in the corresponding states. If S vapour does not follow the ideal gas behaviour, the above equation may be replaced by the (partial) definition equation,

$$\bar{F} - F_0 = RT \log \frac{a'}{a_0},$$

where  $a'$  and  $a_0'$  are defined as the *activities* in the corresponding states. As the pressure of S vapour decreases and approximates to the ideal state, we shall complete the above definition by saying that  $a'$  approaches  $c$ . If we write  $\frac{a'}{a_0} = a$ , an equation defining  $a$ , the *relative activity*, then

$$\bar{F} - F_0 = RT \log a. \dots (2)$$

\* The term "free energy" is used here to mean the quantity  $u - T\phi + pv$ , where  $u$ =total energy,  $\phi$ =entropy,  $p$ =pressure,  $v$ =volume.

At the standard state the value obtained from equation (2) must be zero; hence  $\log a=0$  and  $a=1$ . For an increase of pressure equation (2) gives

$$\left(\frac{\partial \overline{F}}{\partial P}\right)_T = RT \left(\frac{\partial \log a}{\partial P}\right)_T \dots \dots \dots (3)$$

Combining (1) and (3),

$$\left(\frac{\partial \log a}{\partial P}\right)_T = \frac{V_s}{RT}.$$

Integrating this equation from  $P=p_s$ , where  $p_s$  is the pressure of pure S vapour in equilibrium with the condensed phase at the temperature T, to  $P=P$ ,

$$(\log a)_{P=P} - (\log a)_{P=p_s} = \frac{V_s}{RT}(P-p_s), \dots \dots (4)$$

if the compressibility of the solid (or liquid) substance S is sufficiently small that it may be neglected. If the standard state of pure S vapour be chosen as that in equilibrium with solid (or liquid) S at T, then by definition  $(\log a)_{P=p_s}=0$ , and equation (4) becomes

$$\log a_P = \frac{V_s}{RT}(P-p_s).$$

When P becomes large compared to  $p_s$ , this equation may be written

$$\log a_P = \frac{PV_s}{RT}, \dots \dots \dots (5)$$

where P is the partial pressure of the indifferent gas.

Since by supposition the concentration of S vapour in E is small, it may be supposed to conform to the ideal gas laws with sufficient approximation, and thus  $a'=c$  for the pure vapour phase E. Owing to the presence of the indifferent gas in B, which may be at high pressure and concentration, it does not follow that in the gas + vapour phase  $a'=c$ . Introducing an activity coefficient defined by the equation  $a'=f'c$ , then

$$\frac{a'}{a_0'} = a = \frac{f'c}{f_0'c_0},$$

and by putting  $\frac{f'}{f_0'} = f$ , where  $f$  is the relative activity coefficient,

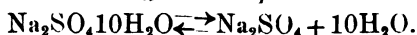
$$a_P = f_P \cdot \frac{c_P}{c_0}, \dots \dots \dots (6)$$

and from equations (5) and (6)

$$\log f_P = \frac{PV_s}{RT} + \log c_0 - \log c_P \dots \dots \dots (7)$$

Hence, if from the experimental data  $c_p$  as a function of  $P$  be known,  $f_p$  as a function of  $P$  can be determined, and the deviation from the ideal gas laws of  $S$  vapour in its admixture with the indifferent gas ascertained.

If  $C$ , in fig. 1, consists of two solid phases possessing a definite equilibrium vapour pressure for a given temperature, *e.g.*  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{SO}_4$ , the calculations and formulæ are analogous to those given above. The reversible reaction occurs according to the equation



If, at the pressure  $P$  and the temperature  $T$ ,  $F_1$  be the molar free energy of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $F_2$  the molar free energy of  $\text{Na}_2\text{SO}_4$ , and  $\bar{F}$  the partial molar free energy of  $\text{H}_2\text{O}$  vapour in its admixture with the indifferent gas, then for equilibrium

$$F_1 = F_2 + 10\bar{F}$$

and

$$\left(\frac{\partial F}{\partial P}\right)_T = \frac{1}{10} \frac{\partial}{\partial P} (F_1 - F_2)_T = -\frac{V_1 - V_2}{10}, \dots (8)$$

where  $V_1$  is the molar volume of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and  $V_2$  the molar volume of  $\text{Na}_2\text{SO}_4$ . From (3) and (8)

$$\left(\frac{\partial \log \alpha}{\partial P}\right)_T = \frac{V_1 - V_2}{10RT}.$$

By a similar reasoning to that employed in the previous case,

$$\log \alpha_p = \frac{V_1 - V_2}{10RT} \cdot P, \dots (9)$$

the standard state being defined as that of pure water vapour in equilibrium with the solid phases at the temperature  $T$ . The compressibilities of the solid phases are small and may be neglected without appreciable error. As

an approximation,  $\alpha_p$  may be put equal to  $\frac{c_p}{c_0}$ ; whence

$$\log \frac{c_p}{c_0} = \frac{V_1 - V_2}{10RT} \cdot P, \dots (9a)$$

and, if  $c_0$  be known, the concentrations at various pressures of the indifferent gas may be calculated with the validity

involved in the assumption that  $\alpha_p = \frac{c_p}{c_0}$ . From equations (6) and (9),

$$\log f_p = \frac{V_1 - V_2}{10RT} \cdot P + \log c_0 - \log c_p, \dots (10)$$

and  $\log f_p$  may be determined as a function of  $P$ , if, from the experimental data,  $c_p$  is known as a function of  $P$ .

As the pressure of the indifferent gas increases,  $f$  will be subject to two influences:

- (a) An intermolecular attraction or association between the molecules of  $S$  vapour and those of the indifferent gas.
- (b) A diminution of the space available for the molecules of  $S$  vapour, owing to the increasing space occupied by the molecules of the indifferent gas.

In the case of a pure gaseous substance these two influences were considered by van der Waals, and are embodied in his well-known equation,

$$p = \frac{RT}{v-b} - \frac{a}{v^2}.$$

If  $p_i$  denote the pressure of a gas, supposed ideal, at the same volume  $v$  and temperature  $T$ ,

$$p_i = \frac{RT}{v},$$

and therefore

$$\frac{p}{p_i} = \frac{v}{v-b} - \frac{a}{RTv}.$$

As  $p$  increases and  $v$  diminishes,  $\frac{p}{p_i}$  will at first diminish owing to the effect of the second term, whilst when  $v$  becomes sufficiently small,  $\frac{p}{p_i}$  will increase owing to the preponderating effect of the first term. The following table ('Thermodynamics,' Lewis and Randall, p. 196) shows this behaviour for Oxygen at  $0^\circ \text{C}$ .:—

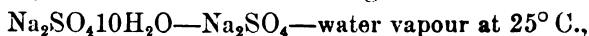
P Atm.	$p/p_i$	Fugacity-coefficient.
50	0.961	0.960
100	0.929	0.925
200	0.91	0.87
400	1.05	0.85
600	1.29	0.90

From the second column it is evident that the ratio  $p/p_i$  for oxygen begins to increase at some pressure between 200 and 400 atmospheres. The third column gives the value of fugacity, a quantity which is closely related to the activity pressure.

coefficient in the preceding. The fugacity coefficient decreases to a minimum value at some pressure between 400 and 600 atmospheres, and then increases. If the vapour of C in E does not obey the ideal gas laws, the activity coefficient would vary with the pressure in this manner. The argument can be applied only to pure gaseous systems, but it seems probable that in the mixture of S with the indifferent gas the first effect of increasing the concentration of the latter would be to decrease the activity of S. The result of this would be a greater increase in the concentration of S with increasing pressure of the indifferent gas than would be given by an equation such as (9 a). It is very probable, therefore, that the first effect of increasing the pressure of the indifferent gas would be to decrease the value of  $\log f$  as experimentally determined.

#### *The Method.*

The system chosen for the investigation was



the indifferent gas used being air. The air was maintained in contact with the sodium sulphate, at constant pressure and temperature, until equilibrium was established between the partial pressure of the water vapour it contained and the dissociation pressure of the solid phases. A small amount of this air containing water vapour was released to atmospheric pressure and the amount of water vapour in a known volume determined.

The pressure was accurately determined by means of a gauge in which a Cailletet tube, mounted in a suitable mercury-filled steel block, was employed. The tube was filled with a known volume of pure hydrogen, and the pressure determined from the diminution of the volume of the hydrogen.

The water vapour was removed from the air in a specially designed condensation tube. It consisted of a U-tube connected to a mercury manometer, in one limb of which was a constant volume pointer. The volume of the condensation tube to the tip of this pointer was accurately determined. The water vapour was removed from the air by passing it through the U-tube, which was immersed in liquid air. While the tube was still maintained at the temperature of liquid air it was closed off from the remainder of the apparatus and evacuated to a pressure of  $1 \times 10^{-6}$  mm. of mercury. The condensation tube was

then closed off from the evacuating system and heated to such a temperature that the water frozen out was completely converted into vapour, and its pressure as such measured. The pressure, volume, and temperature of the water, as vapour, are known, and assuming that at such low pressures (20 mm.) water vapour behaves as an ideal gas with sufficient approximation, its mass may be calculated. The method was carefully tested, and it was found that the error involved was 1 part in 1000.

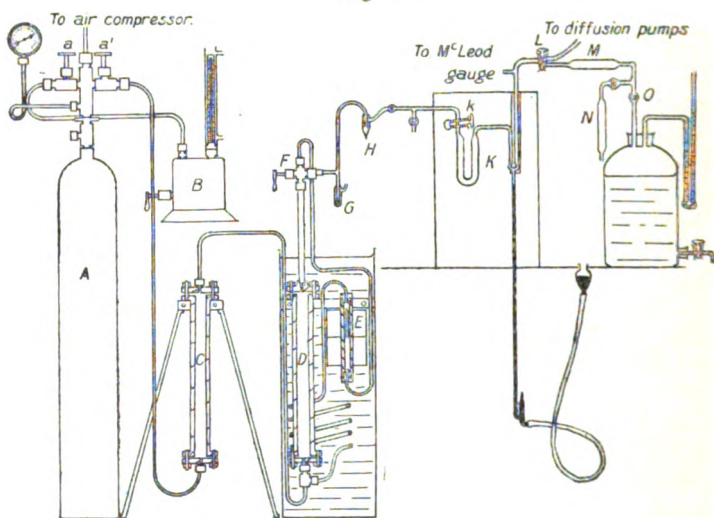
It was found that diffusion alone was not sufficient to establish equilibrium between the partial pressure of the water vapour in the air under pressure and the dissociation pressure of the solid phases with the necessary rapidity, and a device for circulating the air under pressure was employed. The device worked on the principle of the ordinary lift pump with the usual arrangement of valves. The piston was of soft iron, the cylinder of gunmetal and of suitable dimensions to withstand the pressures used. The oscillatory movement of the piston was produced by the agency of a series of solenoid coils wound on the outside of the gunmetal cylinder. The requisite coils were energised by means of a motor-driven commutator. The device was an integral part of the vessel containing the sodium sulphate, and operated in such a way as to provide continuous circulation of the same air upwards through the mixture of the solid phases, downwards through the circulator, to again pass through the sodium sulphate. By the employment of this device equilibrium was readily established within the saturator.

### *The Apparatus.*

The apparatus used is shown diagrammatically in fig. 2. The air was supplied by a motor-driven air compressor. The air, after being compressed, passed through a KOH cylinder from which connexion was made to the apparatus by copper capillary tubing. A is a steel cylinder of about 45 litres capacity with valves, gauges, fittings, and pressure-line leading from the compressor as shown. The valve *a* is a release valve, *a'* closes the connexion between A and the remainder of the apparatus. The arrangement of *a* and *a'* together with the valve in the cylinder A permitted the releasing of pressure from any portion of the apparatus desired, the remaining parts being still maintained at full pressure. The Bourdon gauge was used for the preliminary adjustment of pressure. Accurate readings of pressure

were made on the gauge B connected to the open end of the valve *a*. The cylinder A and the gauges are connected by steel capillary tubing from *a'* to the bottom end of C, which is a steel cylinder containing phosphorus pentoxide. The top end of C is connected by similar steel tubing to the bottom end of a similar steel cylinder D, which was filled with a mixture of equal parts of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  interspersed with sufficient glass-wool to prevent the substance packing tightly together. A second filling was used in which the glass-wool was omitted. The salt used was the purest commercially obtainable and, as measurements of its dissociation pressure at a pressure of one atmosphere agreed

Fig. 2.



with the accepted values, was sufficiently pure for the purpose of such a measurement. A pipe of  $\frac{3}{4}$  inch external diameter with an  $\frac{1}{8}$ -inch bore was fitted into the top end of the cylinder D, to which was attached a reducing valve at F. The circulator is shown at E. The copper capillary from the bottom of the pump was joined at F; the capillary from the top end was about 12 feet long, was coiled into a spiral around D and then joined to a T-piece in the capillary connecting C to D, just below its union to the bottom end of the cylinder D. The long length of capillary tubing is necessary to overcome any heating effect due to the pump and to ensure that the temperature of the air entering D is that of the thermostat. The cylinder D together with

the circulating pump and connexions were immersed in an oil thermostat maintained at  $25 \pm 0.05^\circ \text{C}$ . The projecting portion F was covered by a hood through the side of which the valve handle protruded. A carbon filament lamp inside the hood kept the connecting tubes above the temperature at which condensation could occur.

A glass to metal join at F connects the high-pressure portion of the apparatus to the condensation tube etc. G is a mercury safety valve which prevents excessive pressures developing within the glass tubing. H is a trap to prevent mercury being forced over into the condensation tube, should the connecting taps be inadvertently opened when K is evacuated. K is the condensation tube. It was mounted permanently in an air thermostat provided with plate-glass windows back and front so that readings of pressure could be made. The front was so arranged that it could be removed. The temperature was maintained and controlled electrically. The thermoregulator could be adjusted to temperatures from  $10^\circ$  to  $40^\circ \text{C}$ . Connexions to the diffusion pumps and the McLeod gauge were as shown in the diagram. The tube M was filled with phosphorus pentoxide. A side tube between M and the tap O provided with a tap permitted connexion being made to the tube N, which was open to the atmosphere. The lower half of N was filled with soda-lime, the remainder with phosphorus pentoxide. An aspirator bottle provided with a water manometer and with a thermometer suspended inside completed the apparatus.

### *Experimental Procedure.*

The apparatus to F was raised to the required pressure by means of the air compressor and the pressure-line was cut off at the compressor. The cylinder A is left connected through to D, the needle valve in the gauge B remaining closed except during a reading of the pressure. The oil thermostat and the circulator were maintained in continuous operation. After the thermostat has been at constant temperature, and the air at constant pressure, overnight, the valve F is opened slightly and air from D is allowed to pass slowly through the apparatus, escaping through N. Sufficient air is allowed to escape so that the apparatus from F to k is filled with air released from D, and also that the surface of the glass is in equilibrium with this air. k and F are closed and K is filled with dry air by evacuating the apparatus from k to L and releasing the vacuum slowly through N. K is now immersed in liquid air. When sufficient time has elapsed for the air



in K to have reached the temperature of liquid air and the accompanying decrease of pressure to be adjusted, F is opened slightly and the rate of flow regulated by the rate at which the released air bubbles through the mercury in G. The tap N is closed, O is opened, and finally *k* is opened. Water is then run from the aspirator bottle at from 2 to 3 litres per hour. It was found by experiment that at rates up to 5 litres per hour consistent results could be obtained at any one pressure. The rate of flow of air through K is controlled entirely by the rate at which the water is removed from the aspirator, as it is immaterial during a run whether or not some of the air released at F escapes through G. As a safeguard against any possible leakage between F and *k*, a pressure of from 10 to 15 cm. of water was maintained within the apparatus, so that if there were a leak gas would escape. The escape of air from this portion of the apparatus would make no difference in the final result, but a very small amount of air drawn into the apparatus would give altogether too high a value.

The position of the mercury meniscus in the gauge B is read off on the scale by means of the cathetometer, as is also the position of the top end of the tube, and the pressure determined by reference to the calibration curve for the gauge. The pressure indicated by the Bourdon gauge is also noted.

Sufficient water is run out of the aspirator, so that the amount of water frozen out in K will, when heated to a temperature of  $40^{\circ}\text{C}$ ., give a pressure between 20 and 25 mm. of mercury. When sufficient water has been removed from the aspirator *k* is closed and then F is closed. The pressure from the aspirator to *k* is then reduced to that of the atmosphere by running water from the aspirator. The total number of c.c. of water removed from the aspirator is noted and the temperature of the aspirator read. The pressure is again determined from the gauge B, and the mean of the two readings of the accurate gauge, in which the greatest deviation is never more than 0.2 atmosphere, is taken as the hydrostatic pressure on the sodium sulphate, after correction has been applied for the difference in level between the mercury meniscus in the capillary tube of the pressure gauge and that in the reservoir of the gauge. K is then evacuated very slowly by means of the water-pump and evacuation continued by the diffusion-pumps to as low a value as possible. It is necessary to carry out the first part of the evacuation very slowly, as otherwise some of the minute crystals of ice frozen out in K might be carried

away, and, since the total amount present is very small, such a loss would introduce a considerable percentage error into the final result. The barometric pressure is then read. The mercury is raised into the manometer tube of K, the liquid air removed, and K permitted to come to room temperature. The U is then dried with a cloth and the thermostat closed and set in operation. The pressure in K was measured at successively lower temperatures until the pressures differed by a constant value or were equal to the vapour pressure of water at these temperatures. When such is the case, the pressure measured is the vapour pressure of water condensed on the walls of the tube and is not affected by the adsorption of water from the gas phase. If the pressure is higher than the vapour pressure of water there must be some other gas present, and at the higher temperatures the pressures measured must be corrected for this amount. The temperature is then increased until the pressures read at successively increasing temperatures are increasing proportionally with the absolute temperature. The results are expressed as the number of millimoles of water per litre of dry air measured at the pressure P (the pressure of air in contact with the sodium sulphate). These may be considered as the number of millimoles of water per litre of space in D without appreciable error.

If P is the pressure in atmospheres; V the number of c.c. of water removed from the aspirator at a temperature  $T_v$ ;  $p$  the pressure in K due to water vapour corrected to that of mercury at  $0^\circ$  C. and measured at the temperature  $T_v$ ; (PV) the product of pressure and volume calculated from the data of Amagat (*Ann. de Chim. et Physique*, xix. p. 375, 1880), the value of this product for 1 c.c. of air at a pressure of 1 atmosphere and a temperature of  $25^\circ$  C. being taken as unity; B the barometric pressure corrected to mercury at  $0^\circ$  C. and for the vapour pressure of water at  $T_v^\circ$  C., the moles per litre are calculated as follows. Putting the volume of the condensation tube equal to A, the amount of water expressed as moles equals

$$\frac{273 \cdot A \cdot p}{22410 \cdot 760 \cdot T_v}$$

The volume of air collected, calculated to a pressure of P atmospheres and a temperature of  $25^\circ$  C., equals

$$\frac{298 \cdot V \cdot B \cdot (PV)}{760 \cdot T_v \cdot P} \text{ c.c.}$$

The millimoles per litre of dry air measured at P atmospheres is

$$\frac{1000 \cdot 273 \cdot 1000}{298 \cdot 22410} \cdot \frac{A \cdot T_p P_p}{VB(PV)T_u}$$

*The Accuracy of the Apparatus.*

The various terms in the equation above were determined with the following accuracy:—P to 0.1 atmosphere;  $T_p$  to  $0^{\circ}1$  C.;  $p$  to 0.01 mm.;  $V$  to 5 c.c.;  $B$  to 0.1 mm.;  $T_u$  to  $0^{\circ}05$  C.;  $A$  to 0.01 c.c.; the temperature of the oil thermostat to  $0^{\circ}05$  C. The values of  $(PV)$  are taken as being accurate to 1 in 4000. By differentiating the equation given above and substituting these variations for the corresponding differentials, the probable error of the apparatus is 0.2 per cent.

*The Results.*

The readings obtained in the various measurements are given in Table I. The significance of the various symbols has been given previously with the exception of B.p., which is the barometric pressure as read at the temperature given. Table II. column 2 gives the concentration of water in millimoles per litre of air measured at the pressure P, calculated from the data in Table I. The values calculated from equation (9a) at the corresponding pressures are given in Table II. column 3. The results are shown graphically in fig. 3, in which the values of P are plotted as abscissæ and the number of millimoles per litre as ordinates. The value of the concentration of water in the gas phase when the pressure on the system is that defined as the standard state is given by the horizontal line marked "standard." The calculated values are also given. The plotted values give two distinct curves. From 24.4 to 77.6 atmospheres there are apparently two possible values of the concentration at any one pressure. In this region values have been obtained which fall between these two curves. At all other pressures the values agree within 0.2 per cent., which was the probable error calculated for the apparatus.

The concentrations given in Table II. were obtained from measurements of two fillings of sodium sulphate, the first of which was interspersed with glass-wool, the second in which only the crystals of the hydrated and the anhydrous salt were present. The measurements on the first sample were begun at the higher pressures, above 77.6 atmospheres. The temperature and pressure were maintained constant for

TABLE I.

P Atm.	T <sub>m</sub> °C.	p mm.	T <sub>c</sub> °C.	V c.c.	B.p. at °C.	(P.V.)
2.7	39.0	22.34	13.7	70	757.2 17.5	0.9992
5.1	39.2	20.95	12.5	118	763.6 17.0	.9987
9.3	39.2	22.80	17.0	232	763.8 19.5	.9972
15.1	39.2	24.40	14.9	389	774.3 18.0	.9942
15.4	39.2	26.02	15.8	424	772.5 18.5	.9942
16.5	39.0	24.24	17.5	441	762.8 17.0	.9939
17.3	40.0	16.77	23.0	324	765.5 22.0	.9936
22.3	39.2	21.42	14.9	524	770.5 16.0	.9916
23.8	39.2	19.35	15.3	536	764.3 17.0	.9910
23.9	39.2	18.89	16.3	523	752.2 17.0	.9909
24.4	39.1	19.48	14.3	525	769.8 17.0	.9908
24.6	38.8	18.65	18.2	523	762.1 18.0	.9908
24.7	39.0	16.78	14.2	457	772.0 16.5	.9908
25.0	39.1	30.31	17.1	701	762.7 19.0	.9905
25.2	35.0	17.48	20.1	532	757.4 19.0	.9905
25.2	35.5	17.30	18.1	524	755.4 17.0	.9905
25.3	33.0	17.35	17.2	532	749.0 18.0	.9904
25.4	39.1	28.60	16.1	671	771.0 18.5	.9904
25.6	35.0	16.62	20.0	522	755.4 19.0	.9903
25.7	39.0	18.26	17.2	532	760.4 17.0	.9901
25.8	36.2	20.25	15.0	518	767.7 17.0	.9901
25.8	35.0	17.60	18.4	548	746.5 18.0	.9901
25.8	39.2	19.33	18.2	537	758.4 18.0	.9901
25.9	39.1	24.63	15.5	662	773.4 18.5	.9901
26.0	35.2	16.60	18.8	543	761.2 18.0	.9900
26.2	35.0	16.24	18.2	533	755.4 18.0	.9900
26.3	36.9	21.64	15.2	644	766.7 18.0	.9900
26.9	36.0	18.28	16.5	624	754.5 17.5	.9897
27.7	35.4	19.23	18.5	631	756.9 18.0	.9887
28.1	36.1	16.60	18.2	633	752.6 17.5	.9886
29.4	36.2	19.71	18.1	735	749.3 18.0	.9874
29.9	36.0	23.40	18.6	853	755.3 18.0	.9872
30.4	36.7	21.84	18.7	836	760.6 18.0	.9872
30.6	39.0	23.70	15.5	857	773.0 18.5	.9870
33.1	38.0	16.77	17.8	773	766.3 17.0	.9868
33.2	39.3	24.97	14.9	1064	759.0 18.0	.9868
36.1	37.6	16.71	22.5	825	769.1 21.5	.9864
40.9	39.0	17.87	22.0	1028	772.3 21.0	.9847
41.5	36.6	24.41	19.1	1537	769.7 21.0	.9846
42.8	39.3	27.25	14.3	1566	757.8 18.5	.9842
44.0	38.0	17.15	20.5	1030	769.7 20.5	.9838
45.6	39.3	25.88	15.6	1554	771.8 19.0	.9837
46.4	38.6	15.71	19.7	1028	767.9 19.7	.9834
48.0	36.0	16.08	17.3	1053	749.0 18.5	.9830
49.2	36.5	18.37	20.3	1240	761.2 19.5	.9828

TABLE I. (*continued*).

P Atm.	T <sub>a</sub> °C.	p mm.	T <sub>v</sub> °C.	V c.c.	B.p. at °C.	(P.V.)
55.2	39.2	25.80	18.1	2073	765.0 17.0	0.9811
57.1	39.2	28.84	18.1	2562	750.9 16.0	.9811
• 62.4	39.1	25.60	18.2	2400	760.2 17.0	.9811
64.6	39.6	23.72	19.5	2021	743.6 20.0	.9811
66.7	38.7	23.10	18.3	2305	752.2 16.5	.9811
67.2	39.2	23.16	18.8	2057	769.2 17.5	.9811
67.4	39.9	23.29	16.7	2016	767.4 18.0	.9811
70.0	39.3	25.78	19.0	2663	752.4 18.0	.9810
71.5	38.6	25.40	18.8	2562	772.8 20.0	.9810
72.2	39.5	24.65	18.0	2560	753.0 16.0	.9810
72.5	39.6	25.26	17.4	2570	753.1 16.5	.9810
75.0	39.5	26.56	19.8	2840	757.3 19.0	.9809
75.8	39.2	25.15	17.6	2692	753.4 16.0	.9809
76.3	39.8	26.33	18.9	2760	772.5 21.0	.9808
77.6	39.7	28.13	19.6	3030	754.5 18.0	.9808
81.3	39.6	20.34	20.0	2046	763.4 18.0	.9806
83.8	40.3	23.30	17.7	2610	765.6 16.0	.9806
88.6	39.6	22.81	17.2	2685	761.0 16.0	.9806
92.6	39.2	23.60	17.1	2880	760.0 16.0	.9809
98.4	39.9	24.13	17.2	3070	763.5 16.0	.9818

The volume of the condensation tube was 26.58 c.c. at the following pressures:—2.7; 5.1; 9.3; 15.1; 15.4; 16.5; 22.3; 23.8; 23.9; 24.4; 24.7; 25.0; 25.3; 25.4; 25.7; 25.8; 25.9; 26.3; 26.9; 30.6; 33.2; 42.8; 45.6; 48.0; 64.6; 67.4.

26.75 c.c. at 17.3; 24.6; 25.2; 25.6; 25.8; 26.0; 27.7; 33.1; 36.1; 44.0; 46.4; 49.2; 67.2; 81.3.

And 29.58 c.c. at 41.5; 55.2; 57.1; 62.4; 66.7; 70.0; 71.5; 72.2; 72.5; 75.0; 75.8; 76.3; 77.6; 83.8; 88.6; 92.6; 98.4.

20 hours before a measurement was made. Determinations were made both with increasing and decreasing pressures of air. Proceeding in this manner, the portion of the curve from 100 to 77.6 atmospheres was obtained. At 77.6 atmospheres there was a sharp break in the curve, and to 40 atmospheres the lower curve was obtained. A peculiar effect was observed between 40 and 55 atmospheres. If the pressure were increased from 1 atmosphere to any pressure between 40 and 55 atmospheres, and the temperature and pressure were maintained constant for 20 hours, a subsequent determination of the concentration gave values which fell along the upper linear curve; but if the temperature and pressure were maintained constant for a further

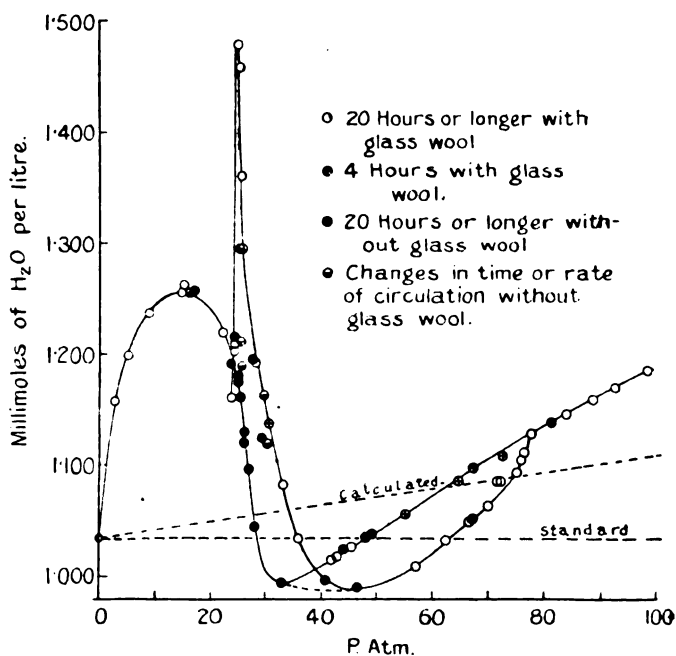
TABLE II.

P Atm.	Millimoles of H <sub>2</sub> O per litre.		log <i>t</i> .
	Found.	Calculated.	
2.7	1.158	1.036	-0.0486
5.1	1.200	1.038	-0.0632
9.3	1.238	1.040	-0.0756
15.1	1.255	1.045	-0.0795
15.4	1.262	1.045	-0.0831
16.5	1.255	1.046	-0.0793
17.3	1.257	1.047	-0.0796
22.3	1.219	1.050	-0.0647
23.8	1.161	1.051	-0.0433
23.9	1.191	1.051	-0.0544
24.4	1.202	1.052	-0.0579
24.6	1.215	1.052	-0.0628
24.7	1.208	1.052	-0.0602
25.0	1.477	1.052	-1.1475
25.2	1.180	1.052	-0.0496
25.2	1.175	1.052	-0.0479
25.3	1.172	1.052	-0.0470
25.4	1.458	1.052	-1.1416
25.6	1.161	1.053	-0.0445
25.7	1.211	1.053	-0.0611
25.8	1.359	1.053	-1.1109
25.8	1.189	1.053	-0.0149
25.8	1.293	1.053	-0.0891
25.9	1.294	1.053	-0.0897
26.0	1.120	1.053	-0.0267
26.2	1.130	1.053	-0.0309
26.3	1.192	1.053	-0.0540
26.9	1.097	1.053	-0.0180
27.7	1.195	1.054	-0.0544
28.1	1.045	1.054	+0.0039
29.4	1.124	1.055	-0.0273
29.9	1.163	1.055	-0.0422
30.4	1.117	1.056	-0.0242
30.6	1.137	1.056	-0.0321
33.1	0.993	1.058	+0.0275
33.2	1.081	1.058	-0.0092
36.1	1.034	1.060	+0.0110
40.9	0.996	1.063	+0.0287
41.5	1.017	1.063	+0.0196
42.8	1.018	1.065	+0.0197
44.0	1.026	1.066	+0.0166
45.6	1.026	1.067	+0.0173
46.4	0.990	1.068	+0.0327
48.0	1.038	1.069	+0.0121
49.2	1.037	1.070	+0.0134

TABLE II. (*continued*).  
Millimoles of H<sub>2</sub>O per litre.

P. Atm.	Millimoles of H <sub>2</sub> O per litre.		log f.
	Found	Calculated.	
55.2	1.059	1.074	+0.0061
57.1	1.008	1.075	+0.0285
62.4	1.032	1.079	+0.0197
64.6	1.085	1.081	-0.0015
66.7	1.049	1.083	+0.0137
67.2	1.051	1.083	+0.0131
67.4	1.097	1.083	-0.0056
70.0	1.063	1.085	+0.0089
71.5	1.085	1.086	+0.0003
72.2	1.085	1.086	+0.0007
72.5	1.108	1.087	-0.0086
75.0	1.093	1.089	-0.0017
75.8	1.104	1.089	-0.0058
76.3	1.111	1.090	-0.0083
77.6	1.127	1.091	-0.0138
81.3	1.136	1.094	-0.0165
83.8	1.144	1.095	-0.0190
88.6	1.158	1.099	-0.0225
92.6	1.169	1.102	-0.0257
98.4	1.184	1.107	-0.0293

Fig. 3.



period of 20 hours, values along the lower curve were obtained. When the pressure and temperature were maintained constant for still longer periods, the values obtained were those on the lower curve. At pressures from 40 to 25 atmospheres the concentrations increased very rapidly with decreasing pressure, reaching a very high maximum at 25 atmospheres. The values from 30 to 25 atmospheres were obtained over a period of 5 days, during which time the thermostat was in operation night and day, maintaining constant temperature throughout this period. Readings were made each day, and the only decrease of pressure during this time was due to the removal of air in making the necessary measurements, and to any leakage in the high-pressure portion of the apparatus. The decrease of pressure was of the order of 0.3 atmosphere in 24 hours. It was thought that some portion of the apparatus might be at fault during this series of measurements, and between each successive measurement of concentration some portion of the apparatus was altered the U-tube K was removed and thoroughly cleaned, the phosphorus pentoxide in the glass portion of the apparatus and in the steel cylinder C was replaced, and fresh soda-lime placed in the tube N; but these various changes had no effect on the concentrations measured. The same conditions of temperature and pressure were maintained from 25 to 23.8 atmospheres, and down to this pressure the concentration of water in the gas phase decreased very rapidly with decreasing pressure. The pressure was then increased to 45 atmospheres, and a measurement at this pressure gave a value agreeing with those already obtained. With decreasing pressure the curve to 25 atmospheres was again obtained. From 23.8 atmospheres downwards the concentrations increased with decreasing pressure, passing through a maximum at 16 atmospheres and then decreasing rapidly to 2.7 atmospheres. Readings below 2.7 atmospheres were not obtained owing to the difficulty of measuring the pressure with sufficient accuracy with the apparatus available. The interpolation of the curve from 2.7 atmospheres to standard pressure is, however, justified from the shape of the curve. Two series of measurements were made from 23.8 to 2.7 atmospheres and agreeing results were obtained. The concentrations gave 4 portions of curves: that from the standard pressure to 23.8 atmospheres with a maximum at 16 atmospheres, that from 23.8 to 77.6 atmospheres with a very high maximum at 25 atmospheres and a minimum at 45 atmospheres (the concentration at this pressure being below the standard



value), the almost linear portion from 77.6 to 100 atmospheres, and a short portion between 40 and 55 atmospheres which appeared to be a continuation of that portion above 77.6 atmospheres. Since, between 40 and 55 atmospheres, the time during which temperature and pressure were maintained constant was the deciding factor on the value of the concentration obtained, it was thought that, by altering the length of time of these conditions between 55 and 77.6 atmospheres, different values of the concentration of water in the gas phase might be obtained. Measurements were made at 55.2, 64.6, 67.4, and 72.5 atmospheres, temperature and pressure being maintained constant for 4 hours before making the determination. The values obtained when plotted gave the upper almost linear curve from 40 to 100 atmospheres. Similar variations were made in the times during which temperature and pressure were maintained constant at pressures between 40 and 2.7 atmospheres, but the results agreed with those obtained after temperature and pressure had been maintained constant for 20 hours or longer. If the concentrations representing a stable state in the system be taken as those which are obtained with temperature and pressure constant over periods of several days, then in the figure the curves representing this stable state will be, that from 2.7 to 23.8 atmospheres, the upper almost vertical portion from 23.8 to 25 atmospheres, the continuous curve from the high maximum at 25 atmospheres passing through a minimum at 45 and again increasing to 77.6 atmospheres, and the portion from 77.6 to 100 atmospheres. The portion from 40 to 77.6 atmospheres, the upper linear curve, would then represent some metastable condition.

The procedure adopted with the second filling, in which the glass-wool was omitted, was to maintain temperature and pressure constant for 20 hours, as before, but to begin at the lower pressures and to trace the curve with increasing pressure. The results were identical with those of the first filling up to 24.4 atmospheres, the concentration increasing rapidly with increasing pressure, passing through the same maximum at 16 atmospheres and then decreasing to 24.4 atmospheres. From 24.4 to 40 atmospheres the values did not, however, agree with those of the first filling; the values now found, instead of increasing with increasing pressure, decreased rapidly passing through a minimum at 33 atmospheres. This portion of the curve was then traced with decreasing pressure, the temperature of the thermostat being maintained constant over a period of 6 days, readings

being made each day; the decrease of pressure being as before due to the air removed in making a measurement, and to any leakage in the high-pressure portion of the apparatus. The results obtained were still those along the lower curve from 24.4 to 33 atmospheres. Between pressures of 40 and 55 atmospheres the values were identical with those of the first filling: namely, with temperature and pressure constant for 20 hours the values along the upper curve were obtained, and with a further period of 20 hours the values along the lower curve were obtained. From 55 to 77.6 atmospheres the results again agreed with those of the first filling; with temperature and pressure constant for 20 hours the values along the lower curve were obtained, whilst with temperature and pressure constant for 4 hours the values along the upper curve were obtained. From 77.6 to 100 atmospheres the results were identical with those of the first filling.

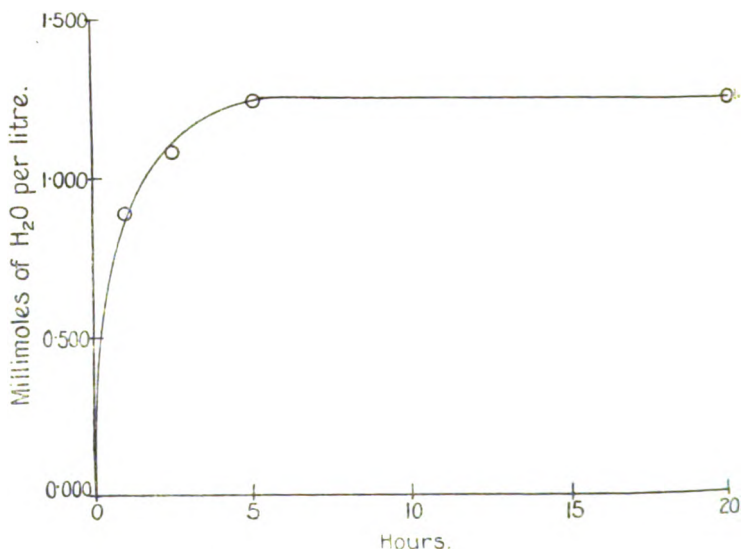
The temperature and pressure were maintained constant at 70 atmospheres for 20 hours; the pressure was then increased to 81.3 atmospheres, maintained constant for 4 hours, and a measurement of the concentration made. The value obtained agreed with all previous measurements. Measurements made with temperature and pressure constant for shorter periods of time gave very low values indicating that equilibrium had not been reached. There was no indication that the conditions represented by the lower curve from 40 to 77.6 atmospheres persisted above the latter pressure. A series of measurements was then carried out at pressures very near to 25.8 atmospheres, in which the time during which temperature and pressure were maintained constant before making the determination as well as the rate of circulation were varied. A similar series was also carried out at 30 atmospheres pressure. The results are shown in Table III.

TABLE III.

P Atm.	Rate of circulation.	Time.	Millemoles per litre.
No. 1.			
25.6	Fast	20 hours	1.161
25.8	Slow	20 "	1.189
25.7	Slow	4 "	1.211
25.8	Slow	1½ "	1.293
No. 2.			
28.1	Fast	20 hours	1.045
30.4	Slow	20 "	1.117
29.9	Slow	4 "	1.163

In the two series in Table III. the rate of circulation as well as the time during which temperature and pressure are maintained constant affect the values of the concentration obtained. In the first series the value at 25.8 atmospheres and  $1\frac{1}{2}$  hours is several percent lower than the value on the upper curve at this pressure; but at 29.9 atmospheres and 4 hours (in No. 2) the value of the concentration is in agreement with those on the upper curve. Another series was carried out at 17.5 atmospheres. The circulation was maintained at the rate which produced the variations in the values of the concentration in the preceding series.

Fig. 4.



Measurements of concentration were carried out with temperature and pressure constant for  $1\frac{1}{2}$ , 3, 5, and 20 hour periods. The pressure (and temperature) had been constant overnight at a pressure of 40 atmospheres, and was reduced to 17.5 atmospheres  $1\frac{1}{2}$  hours before the first determination was made. By this means the concentration of water present in the gas phase is reduced below the standard value. The results are shown graphically in fig. 4, which is an ordinary equilibrium type of curve showing that only the one equilibrium is possible at this pressure. The

accepted value at a pressure of one atmosphere was obtained with both fillings before any readings at other pressures had been made and after each series was completed.

If, as before, the equilibrium conditions be taken as those represented by the concentrations found after pressure and temperature had been maintained constant for 20 hours or longer, then, in fig. 3, the curves representing this stable state will be, that from the standard pressure to 24.4 atmospheres, the lower curve from 24.4 to 33 atmospheres, the lower curve from 50 to 77.6 atmospheres, and that from 77.6 to 100 atmospheres. At 40 atmospheres there may be a curious discontinuity in the curve representing the stable conditions, but it is possible that the curve from 33 to 50 atmospheres may be that represented by the dotted line. The upper linear portion from 40 to 77.6 atmospheres must, as before, be due to some metastable state in the system. A comparison of the results obtained with the two fillings shows a very peculiar effect due to the glass-wool. The curves representing stable equilibrium conditions in the system are identical in both cases from 2.7 to 24.4 atmospheres and from 40 to 100 atmospheres, but from 24.4 to 40 atmospheres, with glass-wool present, the curve representing the stable equilibrium is the upper one with a very high and sharp maximum at 25 atmospheres, while without glass-wool the curve representing the stable conditions in the system is the lower one with a minimum between 30 and 50 atmospheres.

It is beyond the scope of this paper to attempt to explain the anomalies observed, but a comparison with other results is of interest. Pollitzer and Ströbel (*Zeitschr. physik. Chemie*, ex. p. 768, 1924) have determined the concentration of water in the gas phase in equilibrium with liquid water at 50° C. and in the presence of air at pressures up to 200 kg. per cm.<sup>2</sup>. Their results show that the concentration increases with the pressure, the curve obtained when the concentrations per unit volume are plotted as a function of the pressure being very nearly a straight line, and in every case greater than that calculated. The values of  $\log f$  calculated from their data by equation (7) are shown in fig. 5.

Assuming the system in the present research to be



at all pressures, the relative activity coefficient may be calculated. These values of  $\log f$ , calculated from the experimental data by equation (10), are given in column 4,

Fig. 5.

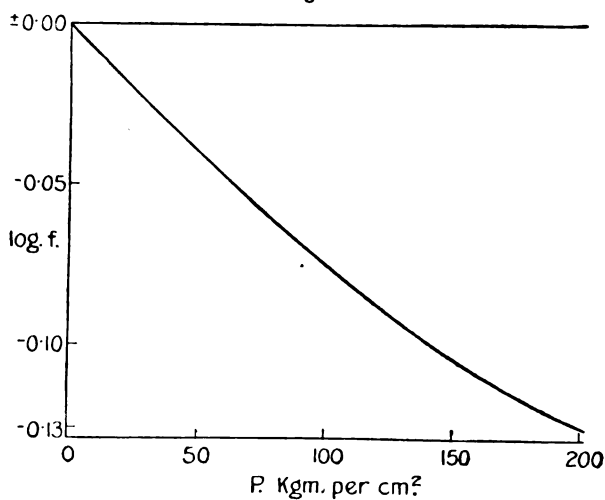


Fig. 6.

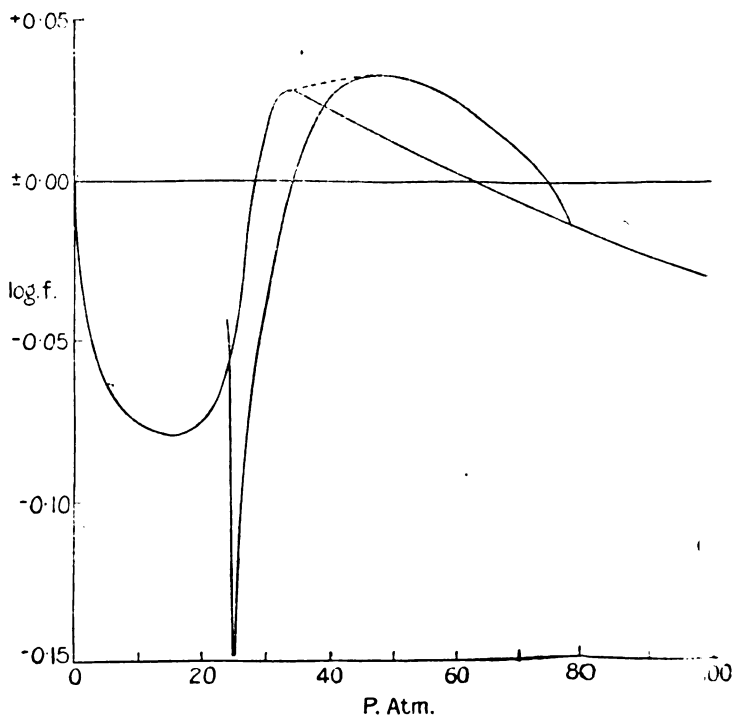


Table II., and are shown graphically in fig. 6. In these deductions the effect of pressure of the indifferent gas on the value of the activity coefficient is taken as being entirely due to the deviation of water vapour from ideal gas behaviour as a result of the increasing density of the indifferent gas. If, however, the two solid crystalline phases (or either of them) should change, then their molar energies and free energies will change suddenly, and the plots of  $\log a$ ,  $\log c$ , and  $\log f$  will show breaks. Further discussion of the phenomenon must be postponed until other hydrate systems have been investigated.

The author wishes to express his thanks to His Majesty's Royal Commissioners for the Exhibition of 1851 for a scholarship during the carrying out of this research, to the Royal Society for a grant to aid in the purchase of apparatus, and to Professor F. G. Donnan, C.B.E., F.R.S., at whose suggestion the research was carried out, for his interest and instructive advice during the progress of the research.

#### *Summary.*

(1) The effect of the presence of an "indifferent" gas on the concentration and activity of a vapour in equilibrium with a condensed phase or system of condensed phases has been discussed thermodynamically.

(2) The relative activity coefficient for the vapour has been defined.

(3) The concentration of water in the gas phase in equilibrium with  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  has been measured in the presence of air up to a pressure of 100 atmospheres.

(4) The relative activity coefficient for water vapour in equilibrium with liquid water at  $50^\circ\text{C}$ . and in the presence of air up to a pressure of 200 kg. per  $\text{cm}^2$  has been calculated from the data of Pollitzer and Strebel.

(5) The relative activity coefficient for water vapour in equilibrium with  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ — $\text{Na}_2\text{SO}_4$  at  $25^\circ\text{C}$ . has been calculated, assuming that the effect observed is entirely due to the deviation of water vapour from ideal gas behaviour as a result of the increasing density of the indifferent gas.

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XLIX. *The Pressure of Radiation.* By W. F. G. SWANN, D.Sc., A.R.C.S., Professor of Physics in Yale University\*.

THE calculation of the pressure on an absorbing or reflecting surface as the result of the incidence of radiation is one of the standard demonstrations of electromagnetic theory. There are two types of proof, one corresponding to that adopted in Planck's 'Wärmestrahlung'†, for example, for radiation reflected from a perfect conductor, and involving an actual calculation of the forces on the currents generated in the conductor by the combined action of the incident and reflected waves, and another proof of a more general type‡, founded upon that equation of electrodynamics which is usually regarded as representing the law of the conservation of momentum. It is the latter proof which is the object of discussion in the present note, and which, in its usual statement, takes a form as follows:—

*The Classical Derivation.*

If **E** and **H** represent electric and magnetic vectors satisfying the electromagnetic equations, then,

$$\iiint \left( \mathbf{E} + \frac{[\mathbf{v}\mathbf{H}]}{c} \right)_x \rho d\tau = - \frac{\partial}{\partial t} \iiint \frac{[\mathbf{E}\mathbf{H}]_x}{c} d\tau + \iint (1p_{xx} + mp_{yx} + np_{zx}) dS; \quad (1)$$

where

$$p_{xx} = \frac{1}{2} (E_x^2 - E_y^2 - E_z^2 + H_x^2 - H_y^2 - H_z^2),$$

$$p_{yx} = p_{xy} = E_y E_x + H_y H_x,$$

$$p_{zx} = p_{xz} = E_z E_x + H_z H_x,$$

where, for simplicity of notation, we have, without loss of generality, confined ourselves to the *x* component of the momentum vector, and where the volume integrals are taken throughout a volume over whose surface the surface integrals are taken, *l*, *m*, *n* being the directional cosines of the outward normal.

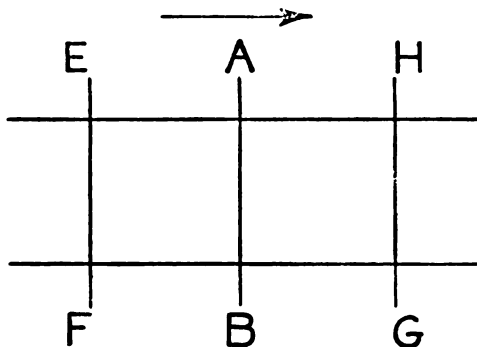
\* Read at the Washington meeting of the American Physical Society, April 25-26, 1924. Communicated by the Author.

† *Wärmestrahlung*, 4th edition, pp. 50-56.

‡ Exemplified, for example, in H. A. Lorentz's 'Theory of Electrons,' pp. 28-29.

Suppose the arrow in fig. 1 represents the direction of the axis of  $x$  and of propagation of a plane wave. Let AB represent the material upon which the wave falls, and let the surface of integration be represented by unit areas EF and HG, and a cylindrical wall bounded in section by the lines EH and FG.

Fig. 1.



Since the wave is plane at EF and HG, the components  $E_x$  and  $H_x$  are zero there. Thus (1) reduces to

$$\iiint \left( \mathbf{E} + \frac{[\mathbf{vH}]}{c} \right)_x \rho d\tau = - \frac{\partial}{\partial t} \iiint \frac{[\mathbf{EH}]_x}{c} d\tau - \iint \left( \frac{\mathbf{E}^2 + \mathbf{H}^2}{2} \right) dS, \quad (2)$$

where  $\mathbf{E}$  and  $\mathbf{H}$  in the surface integrals represent resultant values, and where, in the other integrals it has not been necessary to invoke the question of whether or not  $E_x$  and  $H_x$  are zero everywhere.

Taking the time integral of the vector over a long time  $T$ , we have

$$\int_0^T dt \iiint \left( \mathbf{E} + \frac{[\mathbf{vH}]}{c} \right)_x \rho d\tau = - \left[ \iiint \frac{[\mathbf{EH}]_x}{c} d\tau \right]_0^T - \int_0^T dt \iint \left( \frac{\mathbf{E}^2 + \mathbf{H}^2}{2} \right) dS. \quad (3)$$

The average values may be obtained by dividing throughout by  $T$ .

From here the usual argument is to the effect that if the time  $T$  is sufficiently long, the first term on the right-hand side is sensibly zero compared with the



others since the motions are periodic, with the result that

$$\left[ \iiint \frac{[\mathbf{E}\mathbf{H}]}{c} d\tau \right]_0^T \text{ does not grow without limit with } T.$$

It thus results that

$$\frac{1}{T} \int_0^T dt \iiint \left( \mathbf{E} + \frac{[\mathbf{v}\mathbf{H}]}{c} \right)_x \rho d\tau = - \frac{1}{T} \int_0^T dt \iint \left( \frac{\mathbf{E}^2 + \mathbf{H}^2}{2} \right) dS. \quad (4)$$

The cylindrical wall of the boundary contributes nothing to the surface integral so that the right-hand side of (4) becomes

$$- \frac{1}{T} \int_0^T dt \left\{ \left( \frac{\mathbf{E}^2 + \mathbf{H}^2}{2} \right) \text{ at HG} - \left( \frac{\mathbf{E}^2 + \mathbf{H}^2}{2} \right) \text{ at EF} \right\},$$

since HG and EF are supposed to represent surfaces of unit area.

Thus, if AB is a perfect absorber, so that  $\mathbf{E}$  and  $\mathbf{H}$  are zero at HG and equal to the values  $\mathbf{E}_0$  and  $\mathbf{H}_0$  for the primary wave at EF, we have

$$\frac{1}{T} \int_0^T dt \iiint \left( \mathbf{E} + \frac{[\mathbf{v}\mathbf{H}]}{c} \right)_x \rho d\tau = \frac{1}{T} \int_0^T \frac{(\mathbf{E}_0^2 + \mathbf{H}_0^2)}{2} dt, \quad (5)$$

while if the body AB is perfectly reflecting,  $\mathbf{E}$  and  $\mathbf{H}$  are zero at HG as before, but on account of the occurrence of the incident and reflected waves at EF,  $\frac{1}{2} \iint (\mathbf{E}^2 + \mathbf{H}^2) dS$  has, for this case, twice the value for complete absorption, i. e., twice the value  $\frac{1}{2} \iint (\mathbf{E}_0^2 + \mathbf{H}_0^2) dS$ , so that, for this case,

$$\frac{1}{T} \int_0^T dt \iiint \left( \mathbf{E} + \frac{[\mathbf{v}\mathbf{H}]}{c} \right)_x \rho d\tau = \frac{1}{T} \int_0^T (\mathbf{E}_0^2 + \mathbf{H}_0^2) dt, \quad (6)$$

Thus, the statement is made that, for the case of complete absorption, the pressure is equal to the energy per c.c. in the original wave, while for complete reflexion it is twice this amount.

### *Criticism of the Classical Derivation.*

The vectors  $\mathbf{E}$  and  $\mathbf{H}$  in the surface integrals of the foregoing derivation refer to the total field, and it is as such that  $\mathbf{E}$  and  $\mathbf{H}$  figure in the volume integral of (6), which, of course, only receives contributions from the region occupied by the plate AB. However, the fundamental law which governs the motions of electrons on the classical theory is

the law that each electron moves in such a manner that

$$\iiint (\mathbf{E} + \frac{[\mathbf{v}\mathbf{H}]}{c}) \rho d\tau = 0, \quad . . . . (7)$$

where the integral is taken all over the electron and  $\mathbf{E}$  and  $\mathbf{H}$  refer to the resultant field \*. Thus the left-hand side of (3) is really zero and is not at all representative of the quantity which we wish to associate with the "pressure on the plate

AB." On the other hand, the quantity  $\left\{ \iiint \frac{[\mathbf{E}\mathbf{H}]}{c} d\tau \right\}_0^T$ ,

regarded in its proper light as taken throughout the whole volume, departs very far from the behaviour implied in the foregoing demonstration, in which it was assumed not to increase sensibly with increase of  $T$  for large values of  $T$ . It is quite true that it would have this property if the vectors in it referred only to those associated with the plane wave; but, in the sense of the demonstration they refer to the *total* field, and the quantity in question includes, as part of itself, the electromagnetic momentum imparted to the plate AB by the pressure, which momentum would be evidenced in the motion of the plate if left to itself.

### A Modified Derivation.

(1) *Case where the Plate is Allowed to Move under the Pressure.*—Let us separate the field at each point in space into two parts, the field  $\mathbf{E}_0, \mathbf{H}_0$ , of the primary wave, and the remainder  $\mathbf{E}_i, \mathbf{H}_i$ , which is really produced by the electronic motions in the plate and which manifests itself partly as the electromagnetic waves which cancel the incident wave to the right of AB, or constitute the reflected wave to the left, and partly as the increase of electromagnetic momentum of the plate AB. Thus, having in mind that the left-hand side of (3) is zero, we have,

$$0 = - \left\{ \iiint \frac{[\mathbf{E}_0 + \mathbf{E}_i, \mathbf{H}_0 + \mathbf{H}_i]}{c} d\tau \right\}_0^T - \int_0^T dt \left( \iint \frac{(\mathbf{E}^2 + \mathbf{H}^2)}{2} dS \right), \quad . . . (8)$$

where the square bracket indicates a vector product as

\* See H. A. Lorentz, 'Theory of Electrons,' p. 43.

Strictly speaking the law must be taken in the sense that, at each instant, the volume integral is referred to axes with respect to which the electron is momentarily at rest. However, the elements involved in this matter are not pertinent to the present discussion.

before and where, in the surface integral, we have not dissected the field into the two parts corresponding to the subscripts  $i$  and  $0$ .

Now suppose that, at  $t=0$ , the primary train of waves, which we shall suppose of limited extent, has just reached EF, and that at the end of the time T the tail of it has passed far to the right of GH, and any reflected part has passed far to the left of EF. Then, since at the beginning and end of the time T,  $\mathbf{E}_0$  and  $\mathbf{H}_0$  are zero, the value of the first term on the right-hand side of (8) is

$$-\text{Change of } \iiint \frac{[\mathbf{E}_i \mathbf{H}_i]_x}{c} d\tau \text{ during the time T.} \quad (9)$$

But since, by hypothesis, the tail of the primary wave has passed well to the right of GH at the end of the time T, and since the wave of cancellation has also passed well to the right of GH, and any reflected wave has passed well to the left of EF, expression (9) is left as the representative of the change of electromagnetic momentum of the fields of the electrons in the plate AB as a result of the passage of the train of waves.

As regards the second term on the right-hand side of (8) representing the time integral of  $\frac{1}{2}(\mathbf{E}^2 + \mathbf{H}^2)$  over the planes EF and HG, in the case of total absorption its value is zero over HG and *minus* the time integral of  $\frac{1}{2}(\mathbf{E}_0^2 + \mathbf{H}_0^2)dS$  over EF. In the case of total reflexion it is again zero over GH but is equal to *minus* the time integral of  $(\mathbf{E}_0^2 + \mathbf{H}_0^2)dS$  for the plane EF. Thus we have the conclusion that *if a train of plane waves falls upon a plate for a long time T and is absorbed, the electromagnetic momentum communicated to the plate is the same as that produced by a pressure equal to the energy per c.c. in the plane wave acting for the same time. For total reflexion the effective pressure is twice the above amount.* The line of proof for intermediate conditions is sufficiently obvious, and needs no comment.

The only reason for considering the transition from one steady state of motion of the plate to another which is attained after the radiation has passed completely, is to avoid the awkwardness of definition involved in saying how much of the electromagnetic momentum is to be assigned to the plate, and how much to the radiation field which the plate is continually emitting for the purpose of cancellation of the primary wave to the right or for the purpose of reflexion to the left. Moreover, the result we have calculated is the only one which could have any experimental interest in general for the case where the plate is allowed to move.

As regards the customary proofs, it may be remarked that the sense in which the left-hand side of (1), and so of (6), appears to be understood as representing a pressure on the plate implies that the fields  $\mathbf{E}$  and  $\mathbf{H}$  refer to the fields of the plane waves alone and have nothing to do with the fields produced by the electrons except in so far as they contribute to the waves. As such, however, the left-hand side in question would have no status in electromagnetic theory at all. It is true that equation (1) holds for every field which in itself constitutes a solution of the electromagnetic equations and not merely for the resultant field alone; but the equation is meaningless, or at best hopelessly wrong, unless applied to a situation in which the  $\mathbf{E}$  of the left-hand side of (1) contains in its divergence the quantity  $\rho$  which also occurs in the integral. As a matter of fact the customary derivation endeavours to proceed without utilizing the force equation (7), which is the sole means of determining what happens to the plate dynamically. Equation (1) contains nothing but the circuital relations of electromagnetic theory plus pure algebra. The circuital relations themselves have nothing whatever to say about the motions of charges, so that to attempt to use their consequence (1) to evolve, without the aid of some additional assumption such as (7), an explanation of what happens as regards the motion of a plate upon which radiation falls is to attempt to get something out of nothing\*.

(2) *Case where the Plate is Held Fixed.*—In the case where the plate is supposed held fixed by an external force the argument must take a different form. On the basis of an electromagnetic explanation of things it is necessary to regard the external force as ultimately of electromagnetic nature. For the purposes of a mental picture, we may suppose the plate to be charged, and in spite of the action of the radiation, held fixed through the influence of a statical electric field. For the purpose of the general discussion of the problem, however, no such detailed picture of the mechanism is necessary. The mathematics simply makes use of the fact that, through the combined action of electromagnetic agencies—the radiation and the “external force”—the plate somehow or other finds itself at rest, and it proceeds to discuss the consequences. Nevertheless, as a preliminary, we shall discuss the case where the external

\* See W. F. G. Swann, *Phil. Mag.* ser. 6, xxiii. pp. 86-94 (1912). Also, W. F. G. Swann, “The Fundamentals of Electrodynamics” (Section 1 of Bulletin No. 24 of the National Research Council), pp. 27, 33, and pp. 38-40.

force is brought about by the operation of an external uniform field  $e_x$  on a charge of surface density  $\sigma$  which is supposed spread over the plate.

Equation (7), with  $\mathbf{E}$  and  $\mathbf{H}$  referring to the total field, holds, of course, as before. Thus, the left-hand side of (1) is zero, and the first term on the right-hand side is also zero, since a steady state is postulated, so that we are left with

$$\iint (lp_{xx} + mp_{yx} + np_{zx}) dS = 0. \quad \dots (10)$$

Since  $e_x$  is parallel to the  $x$  axis, the quantities  $E_y$ ,  $E_z$ ,  $H_y$ ,  $H_z$ , still refer to the  $y$  and  $z$  components of the resultant field and also to the field of the wave, modified as it may be by absorption or reflexion.

The charge density  $\sigma$  gives rise to a uniform field  $+\bar{e}_x$ , to the right of the plate, and  $-\bar{e}_x$  to the left, where  $\bar{e}_x$  is given in Heavisidean units, by

$$\bar{e}_x = \frac{1}{2}\sigma. \quad \dots (11)$$

Thus, since the field of the wave to the right of the plate is zero, the use of the expressions following (1) causes (10) to take the form

$$\{E_y^2 + E_z^2 + H_y^2 + H_z^2 + (e_x - \bar{e}_x)^2\} - \{e_x + \bar{e}_x\}^2 = 0, \quad (12)$$

the first expression on the left-hand side of (12) corresponding to the surface integral over one square centimetre of the plane EF and the second expression referring to the corresponding quantity for GH. Thus

$$E_y^2 + E_z^2 + H_y^2 + H_z^2 = 4e_x\bar{e}_x,$$

so that, using (11),

$$\frac{1}{2}(E_y^2 + E_z^2 + H_y^2 + H_z^2) = \sigma e_x. \quad \dots (13)$$

For a case where there is no reflexion, the quantities  $E_y$ ,  $E_z$ ,  $H_y$ ,  $H_z$  refer to the field of the incident wave, so that the left-hand side of (13) represents the energy per c.c. in the incident wave, while the right-hand side represents the electric force per unit area due to the equilibrating field; and the equality of these two as given by (13) expresses, in a rational and understandable way, the precise meaning of the result deduced. For the case of complete reflexion, the left-hand side of (13) corresponds to twice the energy per c.c. in the incident wave, and this is the quantity which, for this case, is equal to  $\sigma e_x$ .

If we do not wish to limit ourselves to the simple case of an equilibrating field of a uniform type operating on a charge

density  $\sigma$ , but desire to leave open the question of just how the equilibrating force (produced by the hand, for example) is to be represented in electromagnetic fashion, subject only to the belief that it is capable of such representation, we proceed as follows :—

Again let us divide the total field into a part  $\mathbf{E}_0, \mathbf{H}_0$ , corresponding to the field of the incident wave and a remainder which we shall call  $\mathbf{E}_k, \mathbf{H}_k$ , since it is not quite the same thing as the field  $\mathbf{E}_i, \mathbf{H}_i$ , which was concerned when the plate was allowed to move, but includes the fields associated with the equilibrating forces. Applying our argument to a region corresponding to a square centimetre of the plate, equation (7) tells us that

$$\iiint \left( \mathbf{E}_0 + \frac{[\mathbf{v}\mathbf{H}_0]}{c} \right) \rho d\tau + \iiint \left( \mathbf{E}_k + \frac{[\mathbf{v}\mathbf{H}_k]}{c} \right) \rho d\tau = 0. \quad (14)$$

Now the field  $\mathbf{E}_k, \mathbf{H}_k$ , in conjunction with the charge density expressed by  $\rho$ , is a solution of the electromagnetic equations, for it is the difference between the total field  $\mathbf{E}, \mathbf{H}$ , which is, of course, a solution of the electromagnetic equations, and the field  $\mathbf{E}_0, \mathbf{H}_0$ , which is also a solution of the electromagnetic equations and has no singularities in the region considered. Thus equation (1) holds for the field  $\mathbf{E}_k, \mathbf{H}_k$ , taken by itself, and we have

$$\begin{aligned} - \iiint \left( \mathbf{E}_k + \frac{[\mathbf{v}\mathbf{H}_k]}{c} \right)_x \rho d\tau &= \frac{\partial}{\partial t} \iiint \left[ \frac{[\mathbf{E}_k \mathbf{H}_k]_x}{c} \right] d\tau \\ &- \iint \left\{ l(p_k)_{xx} + m(p_k)_{yx} + n(p_k)_{zx} \right\} dS, \quad (15) \end{aligned}$$

where the  $p_k$ 's are defined as in the lines immediately following (1), but, of course, with the subscript  $k$ . The region of integration is, as before, that indicated in fig. 1.

Now the first term on the right-hand side of (15) is the rate of increase of the electromagnetic momentum of the field  $\mathbf{E}_k, \mathbf{H}_k$ , for the region indicated by EFHG, and this is zero since the plate is postulated to be at rest\*. It is not the purpose of the analysis to inquire how it may come about that the plate can remain at rest, under the combined

\* Strictly speaking we should speak throughout in terms of averages taken over a long time, which would permit of vibrations of the plate with the period of the light waves. The extension to this line of argument is simple and obvious, though rather cumbersome of expression, and we shall not complicate matters by considering it.

influence of the radiation and the external forces. The business of the analysis is to postulate it and trace its consequences. The first term on the right-hand side of (15) being thus zero, we are left with

$$\iiint \left( \mathbf{E}_0 + \frac{[\mathbf{v}\mathbf{H}_0]}{c} \right)_x \rho d\tau = - \iint \left\{ l(p_k)_{xz} + m(p_k)_{yx} + n(p_k)_{zx} \right\} dS. \quad (16)$$

Now if we assume that the surfaces designated by EF and GH are so far away from the plate that the sole representative of the field  $\mathbf{E}_k, \mathbf{H}_k$  there, is a plane wave, we see that, for the case of complete absorption, the field  $\mathbf{E}_k, \mathbf{H}_k$  cancels  $\mathbf{E}_0, \mathbf{H}_0$  over GH, and is zero over EF. For this case, therefore,

$$\iiint \left( \mathbf{E}_0 + \frac{[\mathbf{v}\mathbf{H}_0]}{c} \right)_x \rho d\tau = \frac{1}{2} \iint \left\{ (\mathbf{E}_0)_y^2 + (\mathbf{E}_0)_z^2 + (\mathbf{H}_0)_y^2 + (\mathbf{H}_0)_z^2 \right\} dS. \quad (17)$$

For the case of total reflexion, the surface EF contributes an equal amount to the right-hand side of (17), so that the result is doubled.

Now the left-hand side of (17) is the quantity which, in the ordinary usage of the terms, represents the force which the field of the incident wave represented by  $\mathbf{E}_0, \mathbf{H}_0$  exerts on unit area of the plate, while the right-hand side of (17) is, of course, the energy per c.c. in the incident wave, and it is the equality of these, for the case of absorption, or the corresponding equality with the omission of the half for the case of reflexion which is the result to which electromagnetic theory leads for the case where the plate is held fixed. The general procedure for cases intermediate between complete absorption and complete reflexion will be sufficiently obvious.

*Cases where the Laws are Not Entirely Electromagnetic.*

For this case, the fundamental equation of electronic motion (7) must be replaced by

$$\iiint \left( \mathbf{E} + \frac{[\mathbf{v}\mathbf{H}]}{c} \right) \rho d\tau + \mathbf{F} = 0, \quad \dots \quad (18)$$

where  $\mathbf{F}$  is a "force" of non-electromagnetic origin. By tracing through the steps of the demonstration immediately preceding, and remembering that (15) still holds, it will

readily be seen that the only effect of the addition of  $F$  is a replacement of the integral on the left-hand side of (17) by this integral plus the result obtained by integrating  $F$  over unit area of the plate. Thus the conclusion reached is that the force per unit area due to the field  $E_0, H_0$  of the incident wave plus the force per unit area due to  $F$  is equal to the energy per c.c. in the incident wave for the case of complete absorption or twice that amount for complete reflexion. It will also readily be seen that, for the case where the plate is allowed to move, the conclusion reached is that, in the complete passage of a train of waves, the momentum gained per unit area of the plate is equal to the time integral of the energy per c.c. in the incident train for complete absorption or twice this amount for complete reflexion minus, in each case, the time integral of the contribution of  $F$  to unit area of the plate.

Sloane Laboratory,  
Yale University.  
August 14, 1925.

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*L. The Variation of the Thermal Conductivity of Gases with Pressure.* By H. GREGORY, B.Sc., D.I.C., Ph.D., and C. T. ARCHER, B.Sc., A.R.C.S., D.I.C., Physics Department, Royal College of Science, S.W. 7 \*.

(1) *Introduction.*

ONE of the earliest consequences, first deduced by Maxwell, of the analysis of the Kinetic Theory of Gases, was that within limits the Thermal Conductivity of a Gas should be independent of the Pressure of the Gas.

The transfer of heat across a layer of a gas whose faces are maintained at different temperatures is effected by the migration of molecules possessing greater kinetic energy, the migration in the opposite direction from the colder layer not being in thermal compensation. Reduction of pressure lowers the molecular concentration but at the same time causes an increase in the free path of the molecule, the two effects being compensating and therefore not affecting the transfer of heat.

Stefan† claimed to have shown this to be true experimentally, but his method of so doing was not at all sensitive and in the light of modern scientific accuracy cannot be

\* Communicated by the Authors.

† Stefan, *Journ. de Phys.* vol. ii. p. 147 (1873).



accepted as an accurate experimental investigation of the effect.

Generally speaking, the measurement of transfer of heat in a gas is effected by the immersion of a heated body in an enclosure dimensionally symmetrical with the body and surrounded by a thermostatic arrangement. The great disadvantage is that associated with such a system, convective losses of heat exist to a greater or less degree with the purely conductive losses, and one of the greatest difficulties is not only to disentangle these losses one from the other, but to design a system in which all convective losses are absent.

In any investigation of the change of conductivity with pressure it cannot be too strongly emphasized that for any method to be susceptible of accuracy and sensitivity two fundamental points must be kept strictly in view :—

- (1) The maintenance at constant temperature of the heated body in the gas, and the arrangement for so doing must be sensitive and easily adjustable during the variation of the pressure conditions, and
- (2) The troublesome elimination of the convective losses which vary considerably with the pressure.

If the constant temperature obligation can be accurately fulfilled, the investigation is considerably simplified. For, taking the example of a wire coaxial with a tube whose external surface is maintained at a constant temperature, and the wire heated by an electric current, it is obvious that if the pressure is lowered, in the absence of convection, we need only to consider the change in the current strength if the wire can be maintained at constant temperature. This not only simplifies the investigation, but enables the whole subject to be treated from the point of view of a qualitative test, while the results lose nothing in the accurate sense of the word. The partial failure of other observers in the subject is attributed to the fact that this important point has not been considered sufficiently.

## (2) *Principle of the Method.*

The experiments of Todd \*, and also those of Hercus and Laby †, involved an experimental system which was free from the complications of convective losses of heat. In the first case, although it would have been possible to maintain

\* Todd, Proc. Roy. Soc. (83) p. 19 (1909).

† Hercus and Laby, *loc. cit.* (95), p. 190 (1918).

the hot body at constant temperature during the variation of the pressure conditions, it was not possible to measure any slight changes in the transmitted heat, which had been shown by Stefan to be small if any at all. In the second case, the disposition of emitting and receiving surfaces, similar to those of Todd, was capable of greater accuracy, and temperatures were measured by a potentiometer system. Such systems were not at all suitable for a test of the variation of conduction with pressure, and after experiments with plate systems, the authors came to the conclusion that the hot-wire method is infinitely superior, both from the point of view of convenience in designing such an apparatus and also by its much greater simplicity of detail and sensitivity. The one trouble with the hot-wire method is that it is difficult to eliminate convective losses of heat, but it has been found that such difficulties are not insuperable.

Weber\*, making use of a vertical disposition of tubes in his hot-wire method, arranged the inlet tubes for the gas in the upper part of the experimental tubes, which necessarily made convective losses inherent in the apparatus, and his experimental system was such that he was unable to maintain the wire at constant temperature during the variation of pressure. The authors found by experiment that with a vertical disposition of tubes it is possible to minimise the convective losses.

It cannot be emphasized too strongly how important the maintenance of the wire at constant temperature is in an investigation of this nature. In the present case, this can be done to a high degree of accuracy, making it possible to base the whole effect of the change, if any, on a change in the current strength.

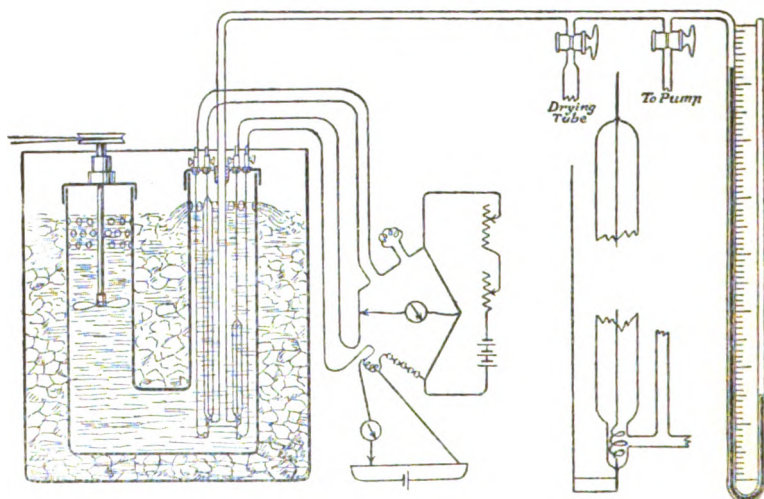
If reference is made to fig. 1, it will be seen that the elimination of the convective losses has been brought about by the observance of the following points :—

- (1) Springs are fixed in the lower part of the tube to maintain the centrality of the wire, and since the temperature distribution here is from above to below no convective losses are possible on this account ;
- (2) The thin wire is continued as far as possible into the closed upper end of the tube ;
- (3) The tube has been made as narrow as possible consistent with the accuracy demanded, again obviating convective loss, since it was found in our main research work that such loss increases rapidly with width of tube ;

\* S. Weber, *Ann. der Phys.* vol. liv. p. 325 (1917).

- (4) The use of very thin wire, diameter 0.004 inch approx.;
- (5) The inlet tubes are at the lower end of the experimental tubes.

Fig. 1.



A main tube constructed on these lines and in conjunction with a similar compensating tube was mounted rigidly and vertically on a brass plate and the whole fixed in one arm of a large brass U-tube, through which a constant stream of water could be forced by means of a propeller worked by an electric motor.

### (3) *Theory of the Method.*

The equation of heat transmission applicable to the above disposition of tubes, assuming that all convective losses are absent, is

$$C^2 R = \frac{2\pi K \theta l}{\log_e r_2 / r_1} + \phi,$$

where  $C$  denotes the current strength,  $R$  the resistance of the effective length  $l$  of thin wire in the main tube which is of uniform temperature  $\theta^\circ \text{C.}$  along its length, the end effects due to heat conducted along the leading wires being compensated by the shorter tube, a point which has been strictly dealt with in our main research;  $r_2$  is the internal radius of the glass tube, and  $r_1$  the radius of cross-section of

the platinum wire,  $\phi$  being the heat loss due to radiation from the wire at the temperature  $\theta^\circ \text{C}$ .

If the temperature of the wire is maintained constant throughout the changes in the pressure of the gas, then  $\phi$  and  $R$  will be also constant, and the change in the conductivity  $K$ , if any, will be indicated by a corresponding change in the value of the current strength necessary to maintain the temperature of the wire constant.

The whole investigation of this effect is therefore one of great simplicity, and demands only consideration of the sensitivity of the experimental system to detect and measure such changes if any occur.

#### (4) *Construction and Arrangement of Apparatus.*

The tubes used in the experimental system were of lead glass supplied by Messrs. J. Powell & Sons (Whitefriars), Ltd. A suitable length of uniform bore was carefully chosen and its dimensions were taken, the internal radius by weighing the quantity of mercury required to fill a known length, and the external radius by means of repeated readings with an accurate slide-callipers.

The thin platinum wire was also carefully chosen as uniform as possible, and its radius found by accurately weighing lengths of about 100 cm. Also the resistance per unit length at different temperatures of the same wire was measured, as in the case of the wire used in the main research work\*. The necessary lengths were then cut and attached to the leading wires and springs, which were made of thick platinum wire, and the complete wires mounted in the tubes, extreme care being taken that the wires were central along the whole length of each tube.

The tubes were next mounted, as explained above, on a brass plate fitting in one arm of a large brass U-tube. This was made from brass tubing 3 inches in diameter, and in the other arm of the U was mounted a large motor-driven paddle-wheel. The whole arrangement was finally fixed rigidly in a galvanized iron tank of about 10 gallons capacity. A plentiful supply of ground ice and a moderately good speed of the paddle-wheel ensured that a copious stream of ice-cold water passed through the U-tube, maintaining the external surface of the experimental tubes at constant and uniform temperature,  $0^\circ \text{C}$ .

After mounting the tubes, the fundamental interval of the effective length of thin platinum wire was next carefully

\* Gregory and Archer, *Proc. Roy. Soc.* cx. p. 91 (1926).

determined, using the temperatures of melting ice and of steam as the fixed points and the Callendar-Griffiths bridge.

The scheme of connexions for the electrical circuit is also shown in fig. 1. The main tube was connected in series with a standard 1 ohm resistance coil in the main arm of the Callendar-Griffiths bridge, which had been calibrated completely previously, and the compensating tube, also in series with a similar and equal standard resistance coil, in the compensating arm of the bridge. The current was supplied by a battery of 2 volt accumulators, and the measurement of the current was carried out by means of a potentiometer connected across the terminals of the standard resistance coil in the main arm of the bridge.

The dimensions, etc. of the apparatus are shown :—

Internal radius of tubes ( $r_2$ ),	0.5144 cm.
External       "       " ( $r_3$ ),	0.605 cm.
Radius of platinum wire ( $r_1$ ),	0.005301 cm.
Resistance of wire at 0° C.,	224.009 cm. bridge wire.
100° 49 C.,	311.365
Fundamental interval of wire between 0° C. and 100° 49 C.,	87.356 cm. bridge wire.
$\log_e r_2/r_1$ ,	4.5751.
$\log_e r_3/r_2$ ,	0.1623.

### (5) *Measurement of Current.*

As stated above, the whole experimental work was based on the detection and measurement of the changes of current required to maintain the wire at a constant temperature. For this purpose an accurate and carefully calibrated potentiometer made by the Cambridge and Paul Scientific Instrument Co., and of the "slide" type, was used. The scale of the slide wire was graduated so that 0.0001 ampere could be measured accurately. Changes of current smaller than 0.0001 ampere could be detected easily though not measured by this instrument, and for this reason use was made of the deflexions of the galvanometer in the bridge circuit to calculate the smaller changes, when they occurred, as indicated below. (See paragraph 7.)

### (6) *Experimental Procedure.*

Briefly, the experimental procedure was as follows :—

The tubes were filled with atmospheric air freed from dust and carbon dioxide and dried by means of phosphorus

pentoxide, and the apparatus operative in maintaining constancy of the external temperature was allowed to circulate for about an hour before any observations were recorded. The bridge setting was fixed to correspond to some temperature previously decided upon, the current was switched on and varied in strength by means of the rheostats in the circuit until the galvanometer indicated a balance. After allowing time for the stationary state to be reached, the current was measured by means of the potentiometer and the pressure readings were taken. The pressure of the gas was then reduced by about 10 cm. of mercury and, after a short interval of time, a test was made to find whether any change in the current strength was necessary to fit in with the new condition of pressure.

An important point at this stage is to decide how far such changes, if any, are due to a possible change in the conductivity or to other variable effects existing in the experimental system. This point has been considered fully below.

The pressure was lowered in this manner in stages of about 10 cm. of mercury and the corresponding current was measured.

After a certain pressure, the mean free path, becoming greater as the pressure of the gas is reduced, begins to approach a value comparable with the distance between the wire and the internal surface of the tube, and there should be at this stage a change in the conductivity due to this effect. This is shown up beautifully in the existing experimental system, the effect occurring in a very gradual manner at first and then, as the pressure is further reduced, in a more marked degree, and at a pressure of about 0.5 cm. (a pressure which depends upon the dimensions of the tubes) undergoes a considerable change.

It is important to notice here that the sensitivity of the experimental system was such that great precautions were necessary to maintain the taps etc. perfectly gas-tight, owing to the rapid change of  $dK/dp$ .

It might also be pointed out that the changes in the conductivity with pressure at very low pressures could be followed easily by the arrangement described, but a difficulty is met with in the fact that it is difficult to measure small pressures with any degree of accuracy, and consequently such observations would be valueless. Though such observations have not been carried out in the present case, arrangements are under consideration, however, to carry out this research separately.

Observations were taken with the wire at different

600 Dr. Gregory and Mr. Archer on the Variation of temperatures, and the results are embodied in the series of tables given below, from which the curves shown in fig. 2

Fig. 2.

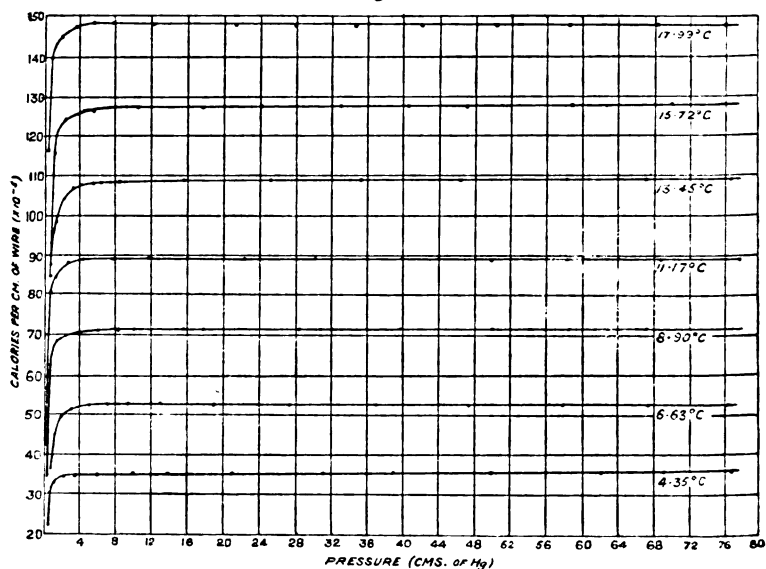


TABLE I.

Temperature of wire,  $17^{\circ}.990$  C.  
 $R/l$  at  $17^{\circ}.990$  C.  $0.12460$  ohm.

<i>p.</i>	<i>C.</i>	<i>W.</i>
76.94	0.2234 <i>avg</i>	0.0014861 <i>cal/sec</i>
68.21	"	"
58.97	"	"
50.16	"	"
42.05	"	"
34.72	"	"
27.99	"	"
21.59	0.2232	0.0014835
12.19	0.2229	0.0014794
7.67	0.2227	0.0014768
5.73	0.2225	0.0014742
3.63	0.2220	0.0014676
1.75	0.2205	0.0014478
0.79	0.2167	0.0013984
0.29	0.1975	0.0011616

have been obtained by plotting the values of the total heat loss at various pressures calculated from the experimental results. The tables are made up of (1) the pressure in cm. of mercury, (2) the current strength in amperes, (3) the total heat loss per cm. of wire calculated from the current

TABLE II.

Temperature of wire,  $15^{\circ}\cdot717$  C.  
R/l at  $15^{\circ}\cdot717$  C.,  $0\cdot12356$  ohm.

<i>p.</i>	C.	W.
76·89	0·2084	0·0012826
70·29	"	"
62·19	"	"
54·97	"	"
47·58	"	"
40·40	"	"
32·92	0·2083	0·0012814
24·01	0·2082	0·0012802
17·72	0·2080	0·0012776
10·45	0·2077	0·0012740
5·40	0·2073	0·0012692
2·24	0·2060	0·0012503
0·60	0·1978	0·0011555
0·28	0·1688	0·0008415

TABLE III.

Temperature of wire,  $13^{\circ}\cdot445$  C.  
R/l at  $13^{\circ}\cdot445$  C.  $0\cdot12252$  ohm.

<i>p.</i>	C.	W.
76·79	0·1921	0·0010805
67·24	"	"
58·04	"	"
46·16	"	"
35·36	"	"
25·22	0·1920	0·0010794
15·79	0·1919	0·0010783
8·22	0·1918	0·0010771
7·56	0·1916	0·0010749
6·52	0·1914	0·0010726
5·26	0·1912	0·0010703
4·04	0·1910	0·0010682
2·86	0·1906	0·0010636
1·54	0·1894	0·0010504
1·02	0·1880	0·0010349
0·44	0·1837	0·0009882
0·22	0·1727	0·0008733



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strength and the resistance per cm. of wire at the appropriate temperature, taking  $J=4.184$ . The temperature of the wire and the resistance per unit length of wire at this temperature are shown at the head of each table.

TABLE IV.

Temperature of wire,  $11^{\circ}171$  C.  
R/l at  $11^{\circ}171$  C.,  $0.12148$  ohm.

<i>p.</i>	<i>C.</i>	<i>W.</i>
77.61	0.1756	0.00089518
68.49	"	"
57.93	"	"
49.67	"	"
39.84	"	"
30.55	"	"
22.61	"	"
11.77	0.1755	0.00089414
9.51	"	"
7.59	0.1754	0.00089316
4.31	0.1750	0.00088911
2.17	0.1742	0.00088102
1.07	0.1726	0.00086488
0.45	0.1663	0.00080290
0.25	0.1207	0.00042286

TABLE V.

Temperature of wire,  $8^{\circ}898$  C.  
R/l at  $8^{\circ}898$  C.,  $0.12044$  ohm.

<i>p.</i>	<i>C.</i>	<i>W.</i>
77.59	0.1575	0.00071399
68.01	"	"
58.72	"	"
49.89	"	"
40.26	"	"
28.14	"	"
17.69	"	"
14.13	0.1574	0.00071307
9.93	"	"
8.03	0.1573	0.00071219
5.97	0.1571	0.00071039
4.03	0.1568	0.00070760
1.97	0.1560	0.00070043
0.77	0.1539	0.00068177
0.33	0.1482	0.00062218
0.09	0.1088	0.00034075

TABLE VI.

Temperature of wire, 6°·626 C.

R/l at 6°·626 C., 0·11940 ohm.

<i>p.</i>	C.	W.
76·56	0·1372	0·00053717
67·46	"	"
57·46	"	"
47·61	"	"
36·81	"	"
27·25	"	"
17·15	"	"
12·75	0·1371	0·00053640
11·03	0·1370	0·00053560
9·19	0·1369	0·00053477
7·01	0·1368	0·00053400
5·05	0·1366	0·00053246
3·15	0·1363	0·00053014
1·43	0·1345	0·00051630
0·63	0·1261	0·00045376
0·33	0·1119	0·00035727

TABLE VII.

Temperature of wire, 4°·352 C.

R/l at 4°·352 C., 0·11836 ohm.

<i>p.</i>	C.	W.
76·67	0·1135	0·00036446
68·84	"	"
61·39	"	"
49·76	"	"
38·97	"	"
31·20	"	"
20·83	"	"
13·54	0·1134	0·00036381
9·17	0·1132	0·00036251
5·97	0·1129	0·00036060
3·13	0·1126	0·00035868
1·79	0·1120	0·00035486
0·79	0·1101	0·00034288
0·37	0·1036	0·00030366
0·23	0·0888	0·00022306

(7) *Absolute Determination of the Conductivity.*

Although it is not claimed that the present investigation is an absolute determination of the thermal conductivity, the conductivity has been calculated from the experimental data and measurements of the dimensions of the tubes and wire, taking the figures shown in Table II., and, as will be seen, differs by less than 1 per cent. from the value of  $K$  arrived at in the more accurate main research on the conductivity of atmospheric air. The values are shown in Table VIII. The small difference is explained by the fact that in the present case the dimensions of the tubes and wire were chosen with a strict view to the elimination of convection, and these dimensions, especially of the wire whose diameter was about 0.004 inch as against 0.006 inch, were not susceptible of the same accuracy of measurement as in the case of those in the main research.

The quantities shown in Table VIII. are (1) the total heat loss per cm. of wire taken from Table II., (2) the total heat loss per cm. of wire after allowing for the loss by radiation, (3) the temperature drop across the glass wall of the tube, calculated as in the main research, (4) the gradient of temperature between the wire and the inner surface of the tube, (5) the actual deflexion of the galvanometer on changing the pressure of the gas, (6) the value of the thermal conductivity calculated from the observations given, and (7) the apparent effect on the conductivity produced by change of pressure, calculated as indicated below.

With reference to columns (5) and (7), it was found during the experiments that on changing the pressure of the gas small deflexions of the galvanometer of the order of 10 scale divisions occurred, indicating that current changes were required, though such changes were too small to be measured by the potentiometer. On this account it was thought necessary to investigate the effect of such changes on the heat transmission. For this purpose the galvanometer deflexions were recorded as shown, and a separate experiment was made to determine the current sensitivity of the bridge system. Repeated observations showed that to produce a galvanometer deflexion of 1 scale division a change of current of 0.000002 ampere was required. Using this value with the deflexions recorded the changes of current were calculated, and thence the effect on the conductivity in each case was found by using the relation

$$\delta K = K \times \frac{2\delta C}{C},$$

where  $\delta C$  is the change of current calculated and  $C$  the current used and measured by the potentiometer.

As the deflexions were sometimes to the right and sometimes to the left, we have considered such changes to be indicative of some change of other conditions existing in the experimental system and not due to any change in the conductivity. Such a change might easily be brought about by a temporary aberration in the constancy of the external temperature, a variation in this temperature of even  $0^{\circ}001$  C. being capable of producing such a deflexion of the galvanometer.

It will be seen from the Table that the effect on  $K$  of these small changes is in the fourth and fifth significant figures only.

TABLE VIII.

W.	W'.	$\theta'$ .	$\theta$ .		K.	$\delta K$ .
0.0012826	0.0012748	0.020	15.697	3 div. right	0.00005914	$+34 \times 10^{-10}$
"	"	"	"	5 "	"	$+57 \times 10^{-10}$
"	"	"	"	0	"	
"	"	"	"	10 div. left	"	$-114 \times 10^{-10}$
"	"	"	"	2 div. right	"	$+23 \times 10^{-10}$
"	"	"	"		"	
0.0012814	0.0012736	"	"		0.00005908	
0.0012802	0.0012724	"	"		0.00005903	
0.0012776	0.0012698	"	"		0.00005890	
0.0012740	0.0012662	"	"		0.00005874	
0.0012692	0.0012614	"	"		0.00005852	
0.0012503	0.0012425	0.019	15.698		0.00005764	
0.0011555	0.0011477	0.018	15.699		0.00005324	
0.0008415	0.0008337	0.013	15.704		0.00003866	

(8) *Conclusion.*

The results of the preceding investigation indicate that, assuming convective losses to be absent, Maxwell's theoretical

prediction of the non-variation of thermal conductivity with pressure is true to the order of accuracy claimed in the experimental work.

With regard to higher pressures, the authors propose to extend the experiments to involve the use of pressures higher than that of the atmosphere.

LI. *On the Nature of the "Critical Increment" of Chemical Action.* By T. CARLTON SUTTON, M.Sc., F.Inst.P.\*

A NUMBER of problems may be attacked by means of either thermodynamics or the kinetic theory, the results obtained by each method being in good agreement with experiment and with one another.

Although hitherto more has been done by means of the thermodynamic than the kinetic method, the latter has supplied information on a number of points which are left indeterminate by the former.

It is the object of the present note to point out that some views recently put forward by Garner† are confirmed when examined from the kinetic view-point, and to indicate that values obtained for the constants in Garner's equations give information of use in the further development of the kinetic theory.

Garner puts forward the view that when two "active" molecules collide, alteration in their chemical nature need not necessarily result, and that there is no reason why a collision between active molecules should not sometimes result in the reformation of the actual reactants, instead of the formation of new compounds as resultants of the collision.

Hinshelwood‡ contends that this is not so, and that whenever the proportion of collisions which result in chemical action (in the ordinary sense of producing other compounds as resultants) is measured it is found to approach unity. This is based on the view that all "activated" molecules have the same energy, and on experimental data obtained from examination of the three reactions §  $2\text{HI} = \text{H}_2 + \text{I}_2$ ,  $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$ , and  $2\text{Cl}_2\text{O} = 2\text{Cl}_2 + \text{O}_2$ .

Since the assumption of similar energy can be challenged, and the accuracy§ of the experimental measurements is

\* Communicated by the Author.

† Garner, Phil. Mag. xlix. p. 463 (1925).

‡ Hinshelwood, Phil. Mag. l. p. 360 (1925).

§ Garner, Phil. Mag. l. p. 1031 (1925).

insufficient for the purpose, his case must be regarded as unproven.

It is here that the view-point of the kinetic theory is of service.

As long ago as 1914, the present author\* (among others) examined the mechanism in accordance with which some molecules behave as "activated" molecules while others do not. A rigid mathematical derivation was then given of the view now generally accepted (quoted in a specialized form by Hinshelwood) that "activated molecules are molecules with specified energies." How many of these exist, and how many collisions take place between them, is determined by the temperature. Measurements to date confirm that the numbers both (i.) of molecules with specified energy and (ii.) of collisions, are in accord with these mathematically derived results and follow classical Maxwellian distribution.

The velocity of a monomolecular† action increases with temperature in a way similar to that of bimolecular actions‡. This fact is used in the paper of 1914 (p. 805) to show that the rotational velocities of the molecules and the velocity of any atom in the molecule (relative to the velocity of the molecule as a whole) accord with the Maxwellian distribution also.

The rotational and internal energy of the molecule must necessarily play a critical role in determining:—

(i.) whether a collision does or does not cause disruption; and

(ii.) whether, once disruption is caused, combination takes place so as to reform the original reactants, or so as to form other compounds as resultants of the collision.

"Activated" molecules have sometimes been defined as those having a specified energy of translation, and sometimes as those having a specified total energy on impact. Further conditions may be imagined also, for instance there

\* Sutton "On the Mechanism of Molecular Action", *Phil. Mag.* xxviii. p. 798 (1914).

† Hurst and Rideal, "Nitrogen Pentoxide" *P. R. S.* 109 A. p. 526 (1925). Hunt and Daniels, "Nitrogen Pentoxide," *J. A. C. S.* xlvii. p. 1602 (1925).

‡ *E. g.*, exponentially as indicated by the Maxwellian distribution. On the other hand, the rate of decomposition of the actual atoms of radioactive elements is independent of temperature. This may be used to show, by means of the kinetic argument, that the component parts of an atom do not move freely in their orbits and that their velocities do not accord with a Maxwellian distribution, a fact which agrees with the recent views of Lorenz and of Millikan.

may be molecules of high rotational energy on the point of centrifugal disruption.

Whatever view may be taken with respect to this, kinetic considerations show that when activated molecules collide, even if they approach in the actual line of centres, their energy distribution is by no means fixed ; there will be some collisions with translation energy suitable for reaction but with rotational and internal molecular energy unsuitable, and, likewise, some collisions with suitable internal, but unsuitable translational, energy. In fact there must be many collisions between these so-called "activated" molecules, which do not result in the formation of new chemical entities, that is to say in chemical interaction in the ordinary sense.

This is substantially the view which Garner has put forward on other grounds.

[It may be contested that "activated" molecules are actually defined as those which do interact on collision. This is a question of words. It is better merely to remark that "activated" is a word that has been inadequately defined, and to point out that in all probability the criterion determining reaction on collision is neither critical translational, nor rotational, nor internal molecular energy, nor that the sum of these energies should exceed a critical value ; the function of these three energies which must equal or exceed some critical value would appear to be more complex and has not as yet been determined.]

A relation between the velocities of the molecules and the velocities of the atoms in the molecules has already been derived \*. Consequently when (with any appropriate definition of "activated") Garner has determined the proportion of collisions that react, *i. e.* his ratio  $kc/(kc - kb)$ , some idea will be gained of the absolute value of those velocities of the atoms within the molecule which are favourable to reaction. Correlation will then be possible with the sizes of the atomic orbits, the period of complete rotation of these orbits, and some of the absorption bands of the substance, especially those in the infra-red.

The author regrets that he has no opportunity of pursuing a research on these lines.

\* Sutton, *loc. cit.*

LII. *The Emission of Electrons under the Influence of Intense Electric Fields.* By The Research Staff of the General Electric Co., Ltd.\* (*Work conducted by B. S. GOSSLING.*)

[Received October 22, 1925.]

ABSTRACT.

THIS paper is primarily an account of experiments on discharge currents observed in well-exhausted tubes and ascribable to the emission of electrons from metal surfaces under the influence of intense external electric fields, of Lilienfeld's autoelectronic discharge.

A general description of the phenomena and in particular of the conditions under which definite numerical data can be obtained is first given.

The numerical data are then collected under the following heads:—

- (a) The rapid continuous variation of the current ( $10^{-9}$  to  $10^{-2}$  amp.) with the applied voltage and the connexion of these variables by a simple empirical relation.
- (b) The nature of the discontinuous irregularities of the discharge.
- (c) The influence of sodium and similar substances on these irregularities.
- (d) The small and generally negligible effect of the temperature of the cathode ( $300^{\circ}$  K. to  $1700^{\circ}$  K.).
- (e) Minimum estimates of the current density ( $10^6$  amps/cm.<sup>2</sup>) and of the surface field ( $5 \times 10^5$  to  $5 \times 10^6$  volts/cm.).
- (f) The gradient of the current/voltage relation.

Schottky's theory of the autoelectronic discharge is then briefly examined in the light of the measurements, and the general conclusion is reached that while the numerical data are not necessarily inconsistent with the fundamental assumption of the theory the question of the actual mechanism of emission is best left open, particularly since the data are definitely inconsistent with any simple application of the theory of thermionics.

(1) **D**ISCHARGE currents of considerable strength, usually several milliamperes, have been obtained by Lilienfeld†† in high-vacuum X-ray tubes, using as the cathode a metal electrode provided with sharp points or edges.

These currents, since they were dependent rather on the form of the cathode and on its distance from the anode than

\* Communicated by the Director.

† *Phys. Ber.* ii. p. 1350 (1921).

†† *Phys. Zeit.* xxiii. p. 506 (1922).



on its temperature or on the degree of evacuation of the tube, were ascribed to the direct action of the applied field on the strongly curved portions of the cathode surface.

The emission of X-rays from the anode was localized in a few sharply defined areas, and there was evidence of emission of softer X-rays similarly localized on the points or edges of the cathode. It was inferred that the discharge took the form of a number of very fine pencils of cathode rays.

The voltage usually employed was 30,000 volts or more, but the discharge could be made to begin at much lower voltages dependent on the material of the cathode, for heavy metals about 5000 volts, and for a caesium cathode a few hundred volts.

Experiments aiming at the proof or disproof of the existence of a critical value of the surface field necessary for the passage of a discharge between metal electrodes in vacuum using high voltages have also been described by Millikan and Shackelford\*†, and by Hayden‡, while Rother§ and Hofmann|| have recently made similar determinations, using moderate voltages and minute gaps between the electrodes.

The conditions under which electrons may be expected to be liberated from the surface of a metallic conductor under the attraction of a strong external field have been discussed in general terms by Schottky in a review of the subject¶, in which he attempts to correlate a large number of phenomena.

Schottky's theoretical treatment is admittedly incomplete owing to lack of suitable experimental evidence; accordingly an account of some further experiments made under conditions analogous to those of Lilienfeld's autoelectronic discharge may be useful. These, while they appear to confirm in general the observations of Lilienfeld, throw light on some features on which he has not touched.

## (2) *Early Observations.*

Since the investigations to be described are chiefly experimental, a general account of the phenomena as we have observed them will first be given.

\* Phys. Rev. xii. p. 167 (1918).

† Phys. Rev. xv. p. 239 (1920).

‡ Jour. Am. I. E. E. xli. p. 852 (1922).

§ Phys. Zeit. xxiii. p. 423 (1922).

|| Zeit. f. Phys. iv. p. 363 (1921).

¶ Zeit. f. Phys. xiv. p. 63 (1923).

Unsupported discharge currents can be produced in any type of well-exhausted thermionic valve without any heating of the filament, provided that a sufficiently high voltage can be applied between the electrodes of the valve without external sparking between the connecting wires. Usually, however, these currents are of an extremely transitory nature; all that can be seen is a flash of fluorescence of the walls of the exhausted bulb, with perhaps a few brilliant white scintillations on the surface of the electrodes, a throw of the pointer of the current indicating instrument, if this is not too sluggish, and, not infrequently, sparking and other forms of breakdown in the high voltage supply circuits. These breakdowns are usually such as require a considerable excess voltage, and therefore indicate that the discharge current was of considerable magnitude and very short duration. The discharges tend to be rather more violent when the cathode filament is cold than when it is incandescent.

In this transitory form the phenomena, though they may become very familiar, do not lend themselves to investigation.

If, however, the valve is first well exhausted, the electrodes being heated either by relatively low voltage thermionic bombardment or by high-frequency induction currents, and if the high voltage is applied through a resistance of the order of a megohm the discharge lasts much longer, often for several minutes, and the main effects can be more closely observed.

These are briefly as follows :—

- (a) If the current is strong enough, currents of several milliamperes being readily obtained, the positive electrode is heated.
- (b) This heating may be extremely local but very intense, *e.g.* holes of diameter one or two millimetres may be melted in a nickel sheet.
- (c) The fluorescence of the glass is also localized in sharply defined patches, representing sections of cones of vertical angle often less than  $10^\circ$ .
- (d) The fluorescent patches may be crossed by sharp shadows of the electrodes and their supports.
- (e) There are local patches of coloured luminescence on the surface of the positive electrode similar in shape to the fluorescent patches on the glass, but succeeded by local heating if the current is maintained at sufficient strength.

- (f) The hot spots on the anode are most frequent where the distance from anode to cathode is smallest, and their occurrence is particularly favoured by points or sharp edges projecting from the cathode.
- (g) The current changes from one value to another at irregular intervals, but clearly increases rapidly with the applied voltage.
- (h) The residual gas in the bulb plays at most a subsidiary part. The better the vacuum the less rapid the variations of the discharge current.

These phenomena are consistent with the supposition of a local emission of electrons from those parts of the cathode system, where the field at the surface is strong; such an emission may thus be a common occurrence given favourable conditions.

### (3) *The Form of the Cathode and other Factors.*

The conditions governing this emission and the nature of various disturbing factors, the operation of which must be defined before theoretical discussion of the results is attempted, were investigated using discharge tubes of various forms; the main types are shown in fig. 1.

Fig. 1.

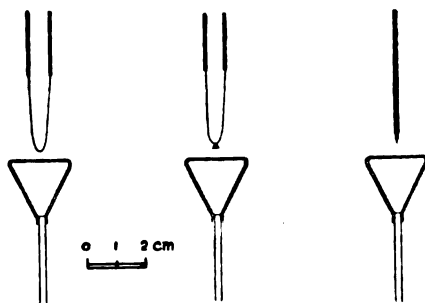


Fig. 1a.  
Loop filament.

Fig. 1b.  
Loop filament  
with brush.

Fig. 1c.  
Single end  
of wire.

The anodes in these tubes were disks 2 cm. in diameter, usually of nickel; with heavy discharge currents, however, even tungsten was readily melted. The distance between cathode and anode at the nearest point was about 0.3 cm.; the electrostatic field due to the anode would thus at this point approximate to that due to an infinite plane.

Comparison of the general behaviour of these tubes

showed that the form of the cathode is of the first importance. Thus, loop filaments of tungsten wire, .02 cm. diameter, gave only transitory indications of discharge even with 60,000 volts between cathode and anode; whereas loops of finer wire, .0015 cm. in diameter, never required more than 25,000 volts for a regular steady discharge. It is important to note, however, that the heating and luminescence of the anode obtained with a loop cathode was always just as strictly local as with pointed cathodes. There was no evidence of a general discharge from all parts of the surface of the wire. The addition of a brush of fine wires of .002 cm. diameter to the thicker loop filaments never failed to produce discharge currents of the order of 1 milliamperes at about 20,000 volts. A single end of .002 cm. wire gave as heavy a discharge as a brush of 50 ends. Very fine points made by etching down the .002 cm. wire to about .0002 cm. (using the wire as anode in electrolysis of ammonia) never required more than 7000 to 10,000 volts for the same heavy discharge.

With a single point cathode the local heating or luminescence of the anode occurred now in one place and now in another, and occasionally in several places simultaneously.

Whatever the form of cathode employed, a general tendency for the discharge to take the form of a single pencil of small vertical angle was always observed.

Changes in the discharge current directly consequent on changes in the cathode temperature were found to be quite small in all these cases. Further observations on this effect will be considered in a later section of this paper.

No very marked differences in the discharge phenomena were observed when the preliminary exhaust by thermionic bombardment of the anode was omitted or left incomplete so that gas could accumulate during the passage of the discharge. At a pressure of .0007 mm. white scintillations on the cathode and changes in position of the hot spot on the anode were frequent.

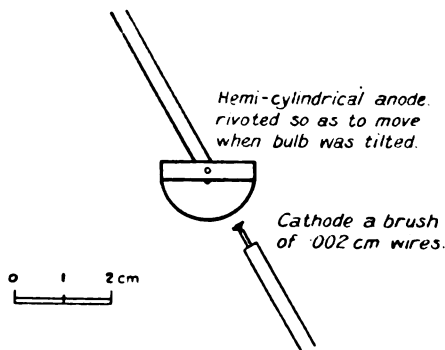
The question whether the anode played any part in the production of the discharge other than that of producing a strong field at the surface of the cathode was investigated by means of a tube having a cylindrical anode, fig. 2, pivoted so that by suitably inclining the bulb different parts of the anode surface could be presented to the cathode. It was found that as the cathode, which consisted of a brush of fine wires, passed over the surface of the anode the hot spot on the anode moved with it, and the discharge current was very little changed. After the tube had been in use some time

the current remained very nearly the same however the anode was moved.

It appears, therefore, that though the effects produced by the discharge on the anode are localized, no special condition occurring locally on the anode surface is a necessary condition of the discharge.

When the current was insufficient to produce a hot spot the corresponding luminescent area on the anode could be observed. This also followed the motion of the cathode, and although the luminescence might change the discharge current did not. Like the hot spot the luminescence is thus a secondary effect. It was observed that melting the anode surface by a heavy discharge destroyed the luminescence of the part melted.

Fig. 2.



Impact of the discharge on the glass gives fluorescence; many cases in which one part of a pencil of discharge strikes the anode, and the remainder the glass, have been observed.

With an open construction, such as a plate anode facing the cathode at two or three millimetres distance, the discharge does not necessarily pass direct to the anode but often by way of secondary emission of some sort from the glass. This may or may not heat the anode; there was a case when the tilting anode became hot on the opposite side from that at which the brush was presented. Again, very often, an ample current with much fluorescence of the glass and no luminescent patches on the anode has failed to produce visible red heat, when a change to smaller current with a luminescent patch and no fluorescence has produced intense heating.

The visible phenomena accompanying the discharge are thus very varied and tend often to obscure rather than reveal its nature. The way in which the current varies with the voltage is, however, absolutely characteristic of this type

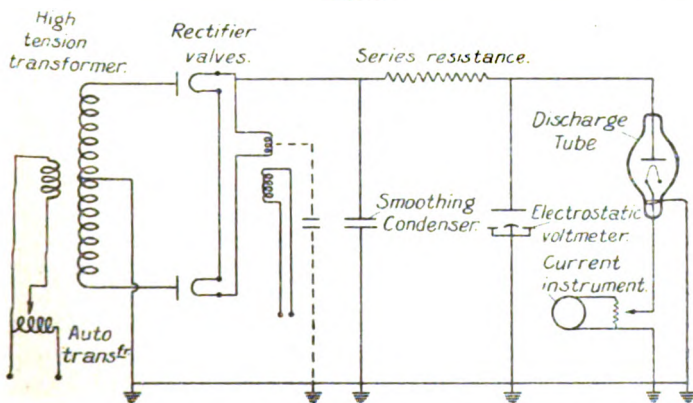
of discharge and enables it to be at once distinguished from any type of gas discharge. When the high voltage is first applied the discharge may set in suddenly with the accompaniment of a scintillation at the cathode. Its subsequent behaviour is, however, much more orderly. The range of variation of the currents observed has been from  $10^{-9}$  ampere to about  $5 \times 10^{-3}$  ampere. Currents of  $10^{-2}$  ampere and more can be obtained, but the melting of the anode and the likelihood of permanent changes at the cathode make continuous observation difficult.

From the lowest values up to about  $10^{-4}$  ampere, the current varies very rapidly with the voltage. If the conditions are steady, as explained later, this variation is perfectly continuous and readings can be repeated whether the voltage is being raised or lowered.

#### (4) *Experimental Arrangements.*

Before we can consider the numerical data a brief description of the various circuit arrangements is necessary (fig. 3).

Fig. 3.



High tension supply circuit etc., using rectified alternating current.

In order to be sure of producing the full field at the surface of the cathode it would perhaps be better to have this electrode at a high negative potential and the anode at earth potential. For reasons of convenience the reverse arrangement was actually that generally adopted. When, however, with any particular tube, a change from the one arrangement to the other was made, there was never any marked change in the discharge current. It may therefore be concluded that the mere difference of potential of the two electrodes sufficiently defines the discharge conditions without reference to other bodies.

In all cases where the smaller currents were being observed the measuring instrument was placed between the low potential terminal of the tube and earth, and for the lowest currents,  $10^{-9}$  ampere or so, an earthed guard-ring round the outside of the bulb near the low potential terminal was used. In any case leakage currents vary so slowly with the voltage that they can only affect the very first readings of any series.

The usual source of high potential was a 50 cycle alternating current transformer with a connexion to the centre point of the secondary winding acting as the negative output terminal. The high tension output terminal was connected to the filaments of two thermionic rectifier valves, the anodes of which were connected one to one end of the secondary winding of the transformer and the other to the other end. The potential between the output terminals thus tended to pulsate sinusoidally at the rate of 100 pulsations per second. A condenser connected across the output terminals eliminated these pulsations provided the output current was not excessive, that is, in the present case, did not much exceed  $10^{-4}$  ampere. For these lower currents the numerical data obtained do not require correction and have therefore a much higher degree of certainty than those for currents of higher value. The effect of the necessary corrections on the data for the higher currents will be further discussed later.

The voltage adjustment was obtained by means of an auto-transformer with numerous tapplings; this had the advantage, particularly in the earlier experiments where the time element was important, of making possible a very rapid repetition of a definite series of voltages, without the temptation to dally over intermediate steps. At the lower voltages the steps of voltage were too large, but here it has since been possible to repeat some series of readings using a direct-current dynamo, and it is found that the more closely spaced intermediate readings so obtained agree well with the scattered readings of the previous observations.

The protecting resistances connected between the discharge tube and the high potential supply had values between 1 and 10 megohms, and consisted of glass tubes containing a saturated solution of copper sulphate crystals in glycerine\*.

In plotting curves allowance is made for the voltage drop in the resistance. When the resistance is in circuit a quick reading electrostatic voltmeter, connected across the discharge tube, affords useful evidence of the steadiness or otherwise of the discharge.

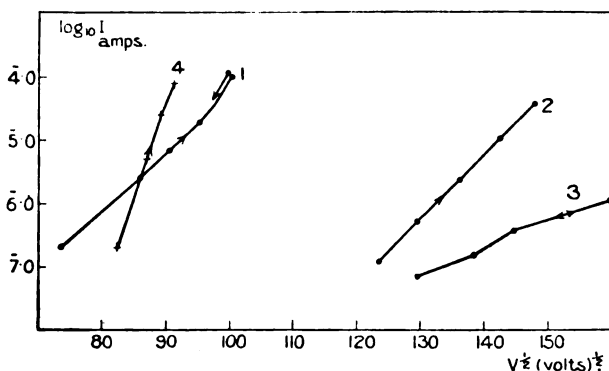
\* A. Gilmour, Phil. Mag. xli. p. 544 (1921).

The currents given are in all cases the arithmetic mean values as indicated by a moving-coil instrument.

(5) *The Relation between Current and Voltage.*

In plotting numerical results the logarithm of the current is taken as ordinate and the square-root of the voltage as abscissa. Our reasons for the adoption of this method of plotting will appear when we come to the theoretical discussion of our results.

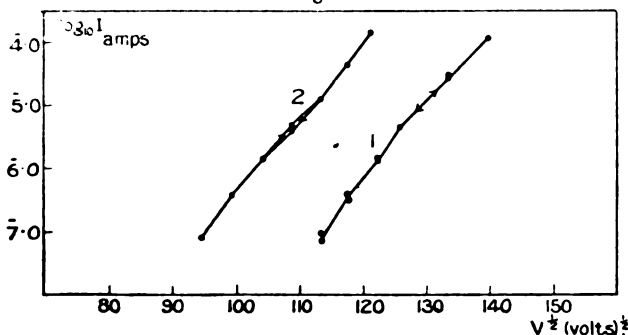
Fig. 4.



Cathode a loop of .0016 cm. wire—electrostatic voltmeter.

- Curve 1. First steady readings, before heating.
2. After heating by auxiliary current to 2300° K.
3. After further heating by auxiliary current to 2300° K.
4. After fracture of loop.

Fig. 5.



Cathodes—Curve 1 a single rounded point of .002 cm. wire.

Curve 2 a brush of .002 cm. wires.

Voltages from transformer peak ( $1.41 \times \text{R.M.S. value}$ ); series resistance 1.7 megohm.

This method of plotting proves illuminating as regards the initial stages of the discharge. Figures 4 and 5, showing



variations of current and voltage for various forms of cathode, indicate that the law of the discharge approximates, in the steady state represented by the cases selected, to the relation :—

$$I = Ae^{pV^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The range of variation of  $V$  is not, however, sufficient to determine accurately the power of  $V$ .

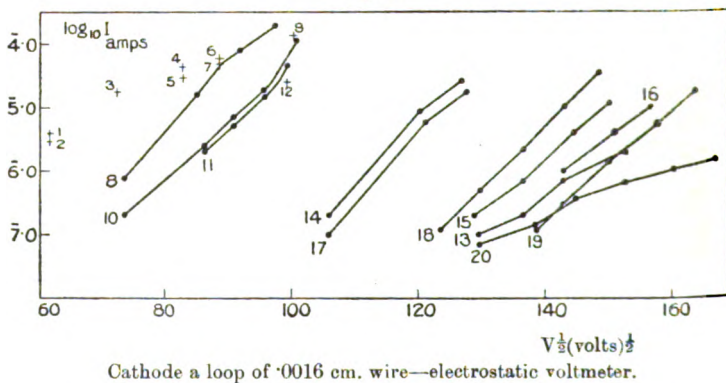
The coefficient  $p$  in the equation, i.e.  $\frac{d \log_e I}{dV^{\frac{1}{2}}}$  is proportional to the gradient of the curves shown.

It appears from these curves, supported by a very much larger number of rather less reliable observations, that a current/voltage relation of this form holds generally from a current value of rather over  $10^{-4}$  ampere down to the limit of observation; a range in the case of the present experiments of 200,000 to 1 in current.

#### (6) *Discontinuous Irregularities of the Discharge.*

The existence of so simple an underlying relation makes it all the more necessary that an explanation should be

Fig. 6.



found for the discrepancies and discontinuities which are so liable to occur among the numerical data. The same method of plotting is found to throw light on the nature of these irregularities of the discharge.

Figure 6 represents a series of characteristic curves taken

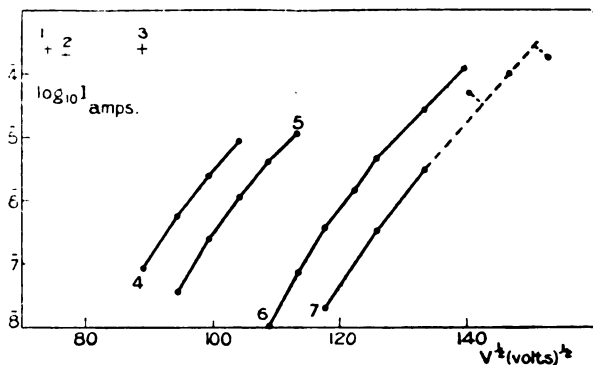
during the life-history of a particular tube. The various points and curves shown are numbered in chronological order. The anode in this tube had been heated during the exhaustion process by high frequency induction currents. The filament, a tungsten wire .0016 cm. diameter, had no current passed through it at any time until the interval between curves 10 and 11. At first spontaneous changes—*e.g.* points 1 and 2, 4 and 5, 6 and 7—were frequent and only single points were obtained; the first definite curve was curve 8. The change from this to point 9 is typical of the effect of an over-rapid increase of voltage at this stage. The resulting new curve 10 is roughly parallel to its predecessor curve 8. The changes between curves 10 and 11 and most of the subsequent changes were induced by heating the filament, each time to a higher temperature; some of the changes were, however, spontaneous. The primary object of the experiments with this tube was to observe the effects of temperature such as will be discussed in a later section of this paper. The room temperature curves here shown illustrate very well the tendency of a given cathode to yield families of curves having approximately the same slope, even though the lateral intervals between the extreme curves of a given family may be such as to reduce the later values of the current at a given voltage to a minute fraction of the initial values.

Each curve shown, except curve 20, represents a single set of readings; none were repeated, but the general direction of the line in each case is confirmed by the parallel curves obtained at other cathode temperatures. Between point 12 and curve 13 the tube was sealed off and the cathode raised to 2000° K. The conditions for curve 13 were unsteady; this curve is included to show the extent of the reverse displacement between curves 13 and 14. The cathode was kept at 2300° K. for two hours between curves 14 and 15 and for a further twenty minutes between curves 19 and 20. Curve 20 was not taken under good conditions, but since the middle pair of points repeated well this curve may be taken to represent a new state of the cathode.

Figure 7 shows a similar history given by a tube having for cathode a single point of wire .002 cm. diameter, which had had been slightly etched by oxidation in fused sodium nitrite in order to remove sharp corners. In this case during the exhaustion the anode was heated by the discharge current itself, and the changes, where not shown as

spontaneous, followed on the passage of heavy currents of from two to five milliamperes for this purpose. As in the

Fig. 7.



Cathode a single point of .002 cm. wire, rounded by etching in  $\text{NaNO}_2$ .

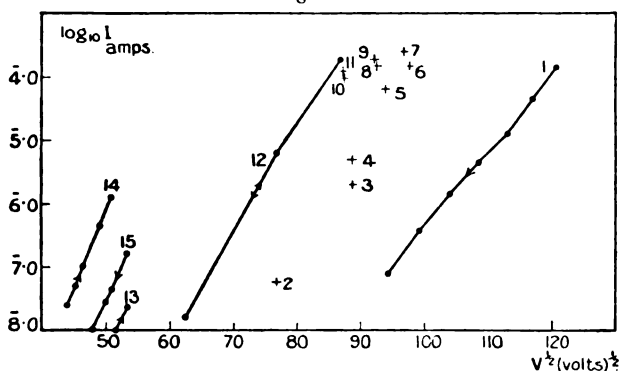
case previously described we have a family of roughly parallel curves, showing successive displacements in the direction of the higher voltages.

#### (7) *Sodium as a Disturbing Factor.*

Displacements in the direction representing an increase in the current at a given voltage do, however, occasionally occur. Changes of this last sort occurring in valves were known to be associated with the possibility of saline deposits due to attempts to clean the electrodes before bombardment, and it was found that in tubes of the types now under consideration a general tendency for the current to increase, instead of diminishing as in the previous case, could be produced by coating the anode with sodium phosphate. The coating was produced by evaporating a drop of saturated solution. On the first passage of the discharge current, or similarly in the early stages of a thermionic bombardment, the surface of the salt nearest the cathode became black. Then when the anode became hot, and only while the anode was hot, the whole cathode system was outlined by a layer of sodium glow. The current increased by several milliamperes and parts of the cathode system became red hot. These effects were clearly due to the bombardment of the cathode by sodium ions liberated from the anode, as in Aston's positive ray technique for sodium and similar substances. This positive current was well observed in one case where the cathode filament was not fine enough to give the autoelectronic discharge, and it was clear that the positive ions were only emitted when the anode, which was heated

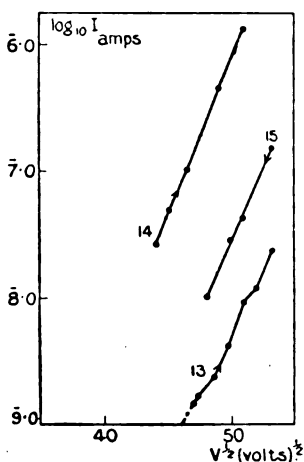
in this case by an auxiliary thermionic bombardment, was at least at a bright red heat. Further evidence of the decomposition of the salt is afforded by the appearance of a green-brown colouration of the nickel anode. The process appears to be a kind of electrolysis *in vacuo*, and it is

Fig. 8 a.



1 to 12 voltage from transformer peak; 13 to 15 from D.C. generator.

Fig. 8 b.



Cathode a brush of .002 cm. wires ;  
anode coated with sodium phosphate.

probable that some action of the same kind will always occur when a layer of salt or even the glass itself, particularly in the neighbourhood of a seal, is subjected to electron bombardment.

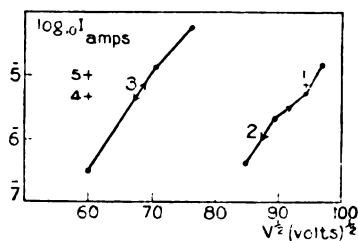
Figures 8 a and 8 b show the extent of the displacement of

the curves in a tube in which sodium phosphate had been decomposed in this way. The sodium glow was only visible at first. Figure 8*b* is on a larger scale; a direct-current dynamo was used as the source of high potential in this case.

The first observations, curve 1, fig. 8*a*, were taken after the tube had been sealed off from the pump, points 2 to 11 after passing heavy currents of a milliampere or more with the sodium glow on the cathode at first, curve 12 after moderate currents of .2 to .5 m.a. without glow. There was an interval of nearly four years between the taking of curve 12 and curve 13. The effect of introducing sodium into the tube is thus in great measure permanent, although it could be still further enhanced by the passage of currents of suitable strength as shown by the later curves.

Figure 9 shows a similar case for a cylindrical cathode used

Fig. 9



Cathode a loop of .0016 cm. wire; anode coated with sodium phosphate.

with an anode coated with sodium phosphate. The cathode being cylindrical, not pointed, the final point 5, 3600 V., indicates a very appreciable current for what is in these experiments a very weak surface field.

The effect of sealing off—unless great care is taken to prevent accumulation of the evolved gases—is always to annul in part the effect of the sodium. A similar effect can be produced by heating the whole bulb to 400° C. while still connected to the pump.

The general tendency where sodium is present in excess is for the curves to be displaced with little or no change of slope in the direction of higher current or lower voltage. It is natural, therefore, to conclude that the sodium is in some way responsible for such displacements, and conversely that the displacement in the reverse direction, illustrated in the cases first described, represents the gradual elimination of traces of sodium or similar substances.

In the case illustrated by fig. 7, a residue of the sodium nitrite used in etching the cathode may have been present initially.

A more general origin of these substances may be the volatilization of alkali compounds from the glass when it is heated to  $400^{\circ}\text{C}$ . in the early stages of the exhaust. This would account for the universal occurrence of these initial displacements, the transitory nature of which so badly masks the main autelectronic effect. Again, O. W. Richardson\* has shown that potassium ions are invariably emitted from a positively charged surface composed of any metal when first heated in a vacuum, and that this potassium emission is sometimes followed by a similar sodium emission.

The displacement in the direction of the higher voltages agrees with Millikan's† account of the progressive rise in the voltage required to produce a spark discharge between metal electrodes placed a few millimetres apart in a good vacuum; it seems probable that sodium or a similar substance may be the "impurity" discussed by him in his later paper.

#### (8) *Temperature effects.*

We may now turn to a more detailed investigation of the effect of the cathode temperature on the autelectronic discharge. The loop filament cathodes used were suitable for observation of the thermionic and autelectronic effects side by side, and throughout these experiments, whenever the temperature was high enough for the thermionic currents to be measurable, these were found to conform to Schottky's relation‡ for the effect of a strong field on a thermionic emission.

The effect of the temperature on the autelectronic discharge was, however, totally different and far more complex. In the first place there is not necessarily any effect at all. In a large number of cases the temperature, as inferred from the heating current passed through the filament, could be raised throughout the range from  $300^{\circ}\text{K}$ . to  $1600^{\circ}\text{K}$ . without appreciable effect on discharge currents of the order of  $10^{-4}$  ampere. Where higher currents of the order  $5 \times 10^{-5}$  ampere were observed the effects, if any, were so small as to be masked by spontaneous variations. Lilienfeld mentions a similar absence of effect on the

\* Proc. Roy. Soc. A, lxxxix. p. 507 (1914); also 'Emission of Electricity from Hot Bodies,' p. 218, Ch. VI. 2nd ed. 1921.

† Loc. cit.

‡ Phys. Zeit. xv. p. 872 (1914).

discharge current when the temperature is lowered to 80° K. by means of liquid air.

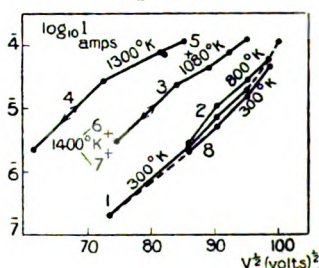
The conditions for this independence of temperature seem to be that the discharge shall be steady, and in particular free from tendency to spontaneous variation in the direction of decreasing current. A tendency to slow, continuous increase of current with the cathode at 1600° K. is a sure indication that subsequent lowering of the temperature will have no effect.

Two cases are particularly remarkable. In both of these a current of  $10^{-5}$  ampere was obtained at 3600 volts, an unusually low voltage for a cylindrical cathode. The one tube (see fig. 9) had been provided with an excess of sodium, and in the other the observations in question were made immediately after the high-frequency heating stage of the exhaust, a condition favourable to at least a temporary sodium effect. Since in both of these cases temperatures up to 1600° K. had no effect, it must be concluded that the sodium effect persists even at such high temperatures, as Langmuir and Kingdon \* have found for thermionic emission from caesium up to 900° K. In both cases, however, a subsequent rise to 2080° K. destroyed the sodium effect in part, and necessitated an increase of the voltage to 7000 V.

The temperature effect, when it does exist, is thus a secondary phenomenon characteristic of the stages of transition in the direction of the higher voltages, such as we have ascribed to the progressive elimination of sodium or similar substances †. This view is supported by a closer examination of such regularities as have been observed.

Figures 10 *a* and 10 *b* show the effect as observed at an

Fig. 10 *a*.



On first heating.

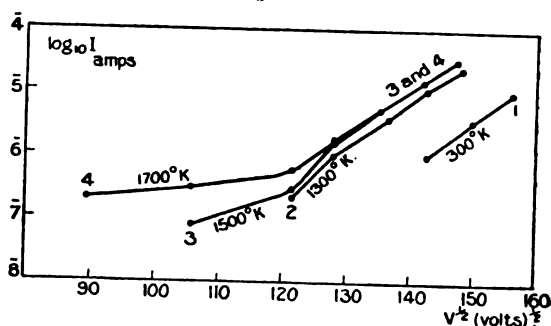
\* Phys. Rev. xxi. p. 380 (1923).

† Compare R. C. Burt's observations, Phil. Mag. xlix. p. 1168 (1925), in the similar effect on photoelectric currents of impurities condensed on liquid air.

early and at a late stage in the transition for a particular cathode. The room temperature curves of fig. 10 *a* are the same as curves 10, 11 of fig. 6, and that of fig. 10 *b* as curve 16 of fig. 6.

In both cases the temperature change was reversible, in fig. 10 *b* very strictly so. Compared with the variation of thermionic emission with temperature the effect is, however, very small. Here we double or treble the absolute temperature, and yet the result is no more than would be produced by a change of a few per cent. in temperature in the thermionic case. The effect of a given rise of temperature is to increase all currents in about the same proportion.

Fig. 10 *b*.



After heating to 2300° K.  
Cathode a loop of .0016 cm. wire.

This on the diagram means a simple displacement of the current voltage curve, with little or no change in slope. This is in marked distinction from the thermionic case, where according to Schottky's law the slope should be inversely as the temperature. The mode of variation of the current with the temperature is not at all simple. As the temperature is progressively increased the effect on the discharge-current is small at first, larger later, and then progressively smaller again. Actually there is an optimum temperature for any given state of the cathode, and if this is exceeded the effect becomes more complicated; higher temperatures produce displacement in the direction of higher voltage, *e.g.* fig. 10 *a*, and the effect is no longer reversible, the room temperature curve being displaced in the same direction. When the temperature is changed there are frequently signs of a small time-lag, illustrated by the first points of curves 2 and 3 (fig. 10 *b*).



With regard to the transition from the thermionic to the autelectronic effect shown in fig. 10 *b*, it must be emphasised that this transition is merely apparent. The curves shown cannot be taken as evidence of physical transition. On the contrary, in each of the four discharge-tubes under observation, while the thermionic bombardment was uniform, the autelectronic discharge was observed to be accompanied by the usual local luminescence or heating of the anode. That the source of the discharge was situated on the filament and not on any other part of the cathode system was made clear by the elongation of the luminescent patches whenever, as sometimes happened, the filament loop went into a sustained vibration of one or two millimetres amplitude transverse to the plane of the loop. What curve 4 (fig. 10 *b*) shows is therefore the addition of an autelectronic current emitted by a small area to a thermionic current of similar total value, but emitted from a far larger area. The autelectronic current increases so rapidly with the field that it very soon masks the thermionic current in the diagram as plotted. All that the two effects have in common is the tendency of the logarithm of the current to vary as a low power of the voltage, which in those cases where the voltage variation covers a sufficient range can be approximately located as the square-root. The coefficient of variation as indicated by the gradients of the current-voltage curves is quite different for the two effects.

### (9) *Observations on Larger Currents.*

In the foregoing detailed consideration of the experimental conditions influencing the discharge, we have confined our attention to currents of  $10^{-4}$  ampere and less. In the majority of the experiments quoted, current readings up to one or two milliamperes were, however, taken, and up to this point continuous curves could usually be obtained. If, therefore, the low-current part of the characteristic was displaced in any particular way, the high current part was similarly displaced. The chief qualitative difference between the two ranges was the greater tendency to spontaneous displacement when the higher currents were passing. If the discharge circuit included a series resistance, and still better if the filaments of the rectifier valves were dulled so as to approach saturation, the extent of the displacement was limited, and currents of the order of 2 milliamperes mean value could be passed for several hours without variation of more than about 20 per cent. When the conditions were such that low voltages, under 7000 V., could be used,

currents of 5 m.a. mean value could be observed, but at higher voltages or with higher currents, the melting of the nickel anode under the intense local bombardment characteristic of the autoelectronic discharge made continuous observation impossible.

In one case where a tungsten anode was used momentary currents of much higher value, about 100 m.a., were obtained.

As regards the form of the current/voltage relation for these higher currents the general conclusion, when due allowance has been made for the effect of pulsation of the applied voltage, is that there are no grounds for supposing that for discharge currents of peak value as great as 30 milliamperes the form of the relation differs in any marked way from that more definitely established for smaller currents of one-tenth of a milliampere or less.

#### *(10) The Current Density at the Emitting Surface.*

None of the experiments described in this paper give any precise information as to the extent of the emitting area from which the discharge pencil emerges from the body of the cathode. Some observations have, however, been made which enable us to set an upper limit to the emitting area, and therefore a lower limit to the current density at the cathode surface. With a cathode consisting of a fine tapered point of final diameter  $\cdot 0002$  cm. a peak current of 30 milliamperes has been obtained. In such a case the emitting area is most probably part of the end of the point. If this is taken to be a hemisphere of diameter  $\cdot 0002$  cm. its area will be  $1\cdot 2 \times 10^{-7}$  cm<sup>2</sup>. Now it occasionally happens that a number of discharge pencils can be seen to be existing simultaneously. In the case of these very fine points as many as four have been seen. The area allotted to a single pencil need not therefore be greater than  $3 \times 10^{-8}$  cm<sup>2</sup>. A current of  $3 \times 10^{-2}$  ampere uniformly distributed over this area corresponds to a current density of  $10^6$  amperes per square cm. This likelihood of a high current density provides an explanation for the brilliant white scintillations on the cathode surface, such as are frequently observed when it is first used. It is not uncommon, particularly if the series resistance in circuit is insufficient, for the scintillations to appear to be extended like the track of a meteor as a bright line, straight or curved, which may on reaching the wall of the bulb return at an angle such as would correspond to the rebound of a flying particle. If we suppose that there are adhering to the cathode surface flakes

of conducting material which are not in good thermal contact with the body of the cathode, the passage of the discharge might easily raise these flakes to incandescence, and even melt them. In this latter case the mechanical force on the cathode surface due to the electric field would tear away the molten particle and project it across the space. Millikan's "hot spark" may represent the form taken by the same effect when the discharge is very powerful.

On this view the scintillations are a secondary effect dependent on a peculiar type of local irregularity of the cathode surface.

A similar though milder local heating must occur in the case of the fine point we have just been considering. Here the root-mean-square of the pulsating current of peak value 30 milliamperes was found to be about 12 milliamperes R.M.S. Now a current of 12 m.a. passed through a long wire of the full diameter  $\cdot 002$  cm. would raise its temperature to about  $900^{\circ}$  K., and would easily fuse a long wire of the diameter, about  $\cdot 0002$  cm., of the end of the point. The temperature actually attained by the point must therefore have been high, unless some limiting agency was present. This may have been the thermal conduction back to the full diameter wire. More probably also the surface cooling effect, which is very important, and perhaps all-important at high current densities, may have kept the temperature down. However, there may have been some temperature rise, for in this, as in many other cases, the effect of passing the heavy current was to displace the characteristic in the same way as those of the loop cathodes when these were raised to a general temperature of  $1500^{\circ}$  K. or so.

#### (11) *The Order of Magnitude of the Surface Field.*

We have seen that the autoelectronic current increases continuously with the applied voltage, and that there is no evidence of a critical value of the voltage at which the discharge suddenly appears. Since, however, we know little about the current density at the cathode in any particular case, we must for the present select arbitrarily a value of the total current at which to compare cases; and since the current varies rapidly with the voltage we can, without any risk of confusion, take any convenient value of the current for this purpose. On grounds of the number of observations available a standard current of  $10^{-6}$  amper-

is most convenient. As we have just seen, it is probable that the current density corresponding to this current is far greater than that usual in the study of thermionic emission.

In the case of the loop cathodes made of drawn tungsten wire of diameter .0016 cm., the extreme values of the voltage for which a current of  $10^{-6}$  ampere has been obtained are about 3000 and 25,000 volts ( $V^{\frac{1}{2}}$  55 to 160).

The field at the surface of a smooth fine cylinder of radius and at voltage  $V$  above its surroundings, assumed remote, being  $\frac{V}{r \log_e \frac{1}{r}}$ , and the value of  $r \log_e \frac{1}{r}$  for  $r$  equal to

$8 \times 10^{-4}$  cm. being  $5.7 \times 10^{-3}$ , the fields corresponding to the voltages given will be  $5.3 \times 10^5$  and  $4.4 \times 10^6$  volts per centimetre.

Since, however, any local irregularity of the surface will result in a local increase of field these numbers must be regarded as minimum estimates. Since again the discharge is observed, in the case of cylindrical cathodes very clearly, not to be uniform over the surface, but on the contrary extremely local, it is very probable that we are concerned with local irregularities of the surface, and therefore higher actual values of the field.

We know also that the lower observed value is associated with the presence of sodium in the discharge tube, but there is some doubt whether the last traces of sodium or similar substances were ever so completely eliminated that we can take the higher value as corresponding to a clean tungsten surface.

It should be remarked, that the mean values of the external field necessary to overcome completely the attraction of the surface, as predicted by Schottky\* from his two methods of calculation, are  $9 \times 10^7$  volts per cm. for a surface of sodium and  $2.8 \times 10^8$  for a surface of tungsten, with respective factors of uncertainty of  $\frac{1}{2}$  to 2 and  $\frac{1}{3}$  to 3. Our values are thus respectively 170 and 57 times smaller. We should expect them to be somewhat smaller because they clearly refer to a case where only a small proportion of the available electrons are actually emitted. The observations on pointed cathodes of various apparent end curvatures indicate as far as can be estimated both a similar range of field and similar extreme values.

\* *Loc. cit.* p 83.

(12) *The Slope of the Characteristic and the Geometry of the Cathode.*

The slope of the current/voltage characteristic as plotted, that is, the value of the gradient  $p = \frac{d \log_e I}{dV^{\frac{1}{2}}}$  is not always the same for a particular cathode, as will be seen in fig. 6; nevertheless, a particular value of the slope may be frequently repeated in a family of curves. The tendency to variation in this respect is greatest in the case of the cylindrical cathodes, perhaps because the much greater area exposed to the strong field provides a greater choice of possible local discharge points. Even with a cylindrical cathode, however, the least value of the gradient, *e. g.* curves 13 and 20 (fig. 6), is as much as  $\frac{1}{3}$  of the greatest, while the greatest gradient is the most common. There is some slight evidence of the existence of definite alternative slopes. If this is true it may perhaps be the result of the crystalline orientation of the local eminences from which the discharge springs.

In the case of the gradient of the characteristic function, as in that of the field-strength for a given current, the values obtained from the pointed cathodes agree with those from the cylindrical as nearly as estimates of the form of the point will allow.

Taking an unweighted average of all observations we obtain:— $\frac{\log_e I}{df^{\frac{1}{2}}} = \cdot 017$ , with maximum values about  $\cdot 026$  and minimum about  $\cdot 009$ ,  $f$  being in volts per centimetre.

The corresponding gradient observed for a general thermionic emission from the same cathode wire was  $\cdot 0013$  in the same units, a very much smaller value.

(13) *Theory.*

Since the most definite theory of the autoelectronic discharge proposed hitherto is that of Schottky, it is of interest to consider if the results recorded can be interpreted according to it.

Schottky's theory is based on an interaction between the external applied field and the internal field which determines the "work-function," or the energy which an electron has to expend in order to emerge. This internal field is supposed to arise from an attraction between an electron and its electrical image in the surface or images in the surface atoms of the metal.

The external field decreases the effective value of the work-function; if  $v_0$  is the normal work-function in the absence of an external field, and if  $f$  is the imposed external field, then  $v$ , the effective work-function, is given by

$$v = v_0 - e^{\frac{1}{2}} f^{\frac{1}{2}}, \quad \dots \quad (1)$$

where  $e$  is the electronic charge.

There are good grounds for supposing that Schottky's principle, expressed by (1), must enter into the explanation of any electron emission effect which is influenced by the surface field; for the agreement of the values of the work-function derived from phenomena so different as the thermionic and photoelectric effects indicates that the work-function is a property of the surface in relation to the emitted electron and is not concerned with the actual mechanism of emission.

We shall in the first place consider whether the aut-electronic effect has anything in common with the fact predicted and observed by Schottky\* that a thermionic current increases considerably if a sufficiently strong field is applied.

According to Richardson's theory of the thermionic effect the electron current  $I$  flowing from the surface at temperature  $T$  can be expressed by

$$I = A T^{\frac{2}{3}} e^{\frac{-v_0}{kT}} \dots \quad (2)$$

Since we shall be concerned only with rough numerical values, it will be permissible to neglect the variation of  $T^{\frac{2}{3}}$  compared with that of  $e^{\frac{-v_0}{kT}}$  and to write

$$I = A' e^{\frac{-v_0}{kT}}.$$

There are other formulæ for the thermionic effect besides (2) which would give us a similar approximate relation.

$$\text{Now by (1)} \quad I = A' e^{\frac{e^{\frac{1}{2}} f^{\frac{1}{2}} - v_0}{kT}} \dots \quad (3)$$

Here if  $T$  is constant we have

$$\log_e I \propto f^{\frac{1}{2}} + \text{constant} \dots \quad (4)$$

Schottky has confirmed this relation experimentally for thermionic emission in a case where  $e^{\frac{1}{2}} f^{\frac{1}{2}}$  was very much smaller than  $v_0$ , and some observations of thermionic

\* *Jahrb. d. Radioact. u. El.* xii. p. 200 (1915).

emission made in the course of our experiments are in agreement with his results (*cf.* curve 4, fig. 10 *b*).

Our measurements, so far as the relation (4) is concerned, are consistent with this application of the theory although, as already mentioned, the accuracy is not so great that they can be held to confirm it. They are, however, completely inconsistent with any such variation of the current with the temperature as is given by (3). A simple numerical calculation of actual values of the exponent in (3) shows this at once.

If (4) represents our measurements at all it does so while  $f$  varies in the ratio of 2 to 1; the assumption of any smaller variation is still more unfavourable to the possibility of consistency. Let us determine the maximum possible effect of such a variation in  $f$  on the exponent. The variation of  $f$  will have more effect the larger the ratio of  $\epsilon^{\frac{1}{2}} f^{\frac{1}{2}}$  to  $v_0$ . Let us suppose then that the upper value of  $f$  makes  $\epsilon^{\frac{1}{2}} f^{\frac{1}{2}}$  equal to  $v_0$ . The lower value of  $f$  will now give a value of the numerator of the exponent less than  $v_0$ , the value where there is no field, in the ratio  $1 - (\frac{1}{2})^{\frac{1}{2}}$  to 1, i. e., 0.3 to 1.

The effect of such a change can be seen at once if we suppose it due to an increase in the denominator instead of a decrease in the numerator.

A reduction in the same ratio would have occurred if the temperature  $T$  had been increased in the ratio 3.3 to 1, that is, from a room temperature value of 300° K. to 1000° K. Such an increase of temperature would not produce any measurable thermionic emission even from the whole area of the cathode; nor, therefore, should the application of our field.

Further, if we heat the cathode generally to 1500° K. and apply the field the new value of the exponent will correspond to a temperature of 5000° K.

With a change in the exponent corresponding to a change of temperature from 1000° K. to 5000° K. the thermionic emission from tungsten would increase  $10^{18}$  times, so therefore should the current emitted under the influence of the field when the cathode is raised from room temperature to 1500° K.

What we have found in our experiments is that measurable currents can be obtained from a small area of the cathode and that there is no certain change consequent on heating from 300° K. to 1500° K. There is thus complete inconsistency between our observations on the autoelectronic

current and the relation (3), and therefore with any extension to lower temperatures of Schottky's modification of the theory of thermionic emission.

Since our observed current/voltage relation is of the form (4) it is of course possible to calculate the value in that relation of the coefficient corresponding to  $kT$  in (3).

It may perhaps be of speculative interest to do so. Using our observed value of the gradient  $\frac{d \log_e I}{df^{\frac{1}{4}}}$  and a correction factor of 50 for the true value of the field—as we shall shortly explain—our maximum estimate of the value of this coefficient lies between the limits  $1.0$  and  $2.8 \times 10^{-12}$  erg, and is most probably about  $1.5 \times 10^{-12}$  erg.

Expressed in electron volts these quantities become  $0.6$  to  $1.8$  volts, probably about  $1.0$  volt, or, dividing by  $k$ , as hypothetical temperatures  $4800^\circ \text{K.}$  to  $14,000^\circ \text{K.}$  probably about  $7500^\circ \text{K.}$

This, however, is a parenthesis of no immediate utility, since (4) is and remains an empirical relation.

Returning to the main question, if  $e^{\frac{1}{4}} f^{\frac{1}{4}}$  is greater than  $v_0$ , the current will on Schottky's theory be independent of the temperature and of the kinetic energy of the electrons in general, for this will then no longer be required in order to make them emerge. Schottky contemplates such a case, and uses it to obtain an estimate of  $f$ , as we shall shortly do.

He cites as possible factors limiting the current, the space charge outside the range of the molecular fields and, possibly, the flow of the electrons through the metal to the point of emergence. Neither of these limitations would be expected to cause the current to vary so rapidly with the field as it does in our experiments; but since he does not carry the theory to the point of making any definite prediction of the relation between the current and the field in these circumstances, this objection perhaps should not be stressed. The only test that can be applied now is whether the measured values of the field are consistent with  $v < 0$  and the known values of  $v_0$ .

If  $f$  were taken to be the value of the field over the general surface of the cathode, its value would be far too small. But since the discharge is localized in a few isolated spots this assumption is improbable; it is much more probable, as Schottky supposes, that there are sharp points at these spots which increase greatly the local values of  $f$ . On this view we have no direct way of estimating the local value of  $f$ , but the following indirect method seems permissible.



According to Schottky's theory, the spontaneous variations of the current are due either to variations of  $f$  or to variations of  $v_0$ . Since the presence of sodium or other electropositive substances seems one of the main factors determining the variations, it is natural to attribute them to changes in  $v_0$ . Indeed, we may assume plausibly that the highest and lowest fields required to produce a given current from the same point correspond to the values of  $v_0$  characteristic of tungsten ( $v_1$ ) and of sodium ( $v_2$ ). We may further assume—this is less plausible, but the displacement of the curves without change of slope supports it—that the change from a tungsten to a sodium surface is accompanied by no change in the geometrical form of the surface, and by no change of the relation of  $f$  to  $v$ , the voltage between the electrodes. Let us then compare the fields,  $f_1, f_2$ , required to produce the same current for the different values  $v_1, v_2$  of the normal work function.  $f_1/f_2$  is known from the ratio of the measured voltages; and we have

$$\epsilon^{\frac{1}{2}} f_1^{\frac{1}{2}} - v_1 = \epsilon^{\frac{1}{2}} f_2^{\frac{1}{2}} - v_2$$

or

$$f_2 = \frac{(v_1 - v_2)^2}{\epsilon} \left[ \left( \frac{f_1}{f_2} \right)^{\frac{1}{2}} - 1 \right]^2.$$

Values of  $f_1/f_2$  ascribable to change in the normal work-function have been observed as high as 4/1. Taking the value of  $v_1$  for tungsten as 4.5 volts and that of  $v_2$  for sodium as 2.0 volts we obtain for the value of  $f_2$   $1.5 \times 10^5$  e.s.u. per cm., i. e.  $4.5 \times 10^7$  volts per cm. Now for any of the forms of cathode we have used the value of  $f_2$  calculated from the applied voltage and the general form of the cathode varies between  $4 \times 10^5$  and  $2 \times 10^6$  volts per cm. according to the value of the current.

It appears then that if the conditions do correspond to values of  $v$  approximating to 0, the points from which the discharge proceeds must be so sharp that the local field is about 100 times greater than the general field. This conclusion is perhaps not wholly impossible in itself; Schottky\* estimates that points may increase the local field 10 times, but there does not appear to us anything in his argument which necessarily sets a limit at this value.

While, therefore, our experiments are not necessarily inconsistent with the basis of Schottky's theory, we do not think that it can be said to derive any additional support

\* *Loc. cit.* p. 78. There is, apparently, a repeated misprint of  $2k$  for  $2^k$  here.

from them. We have no extension of his theory nor alternative theory to propose, not because none is imaginable, but rather because we cannot find any which can be supported by our experiments. Thus, it is not impossible to deny the assumption made throughout the foregoing argument, that the temperature of the spots from which the discharges proceed is the same as that of the main portion of the cathode; sharp points may be heated by the discharge itself until they are capable of a normal thermionic emission; some support for this view might be found in the scintillations that were mentioned in section (10). On the other hand, as we have seen, local emission currents have been observed sufficient to have fused the whole cathode, and yet the sharp point supposed responsible for the emission was little affected and certainly not destroyed.

Again the whole explanation may lie deeper and have to be sought, as Schottky suggests, in terms of space lattices or quantum orbits of the electrons in the metal rather than in terms of a mean kinetic energy. The discussion of these possibilities is, however, best postponed until further facts are available.

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LIII. *The Determination of Minima-Maxima Forces in certain Problems of Dynamic Balance.* By P. FIELD FOSTER, B.Sc., University College, Cardiff, and J. F. BAKER, B.A.\*

CERTAIN problems in dynamic balance require the determination of the smallest maximum value of a rotating force vector and the corresponding angle, resulting from the composition of a vector  $\alpha = P\left(\cos \theta + \frac{1}{n} \cos 2\theta\right)$  with a vector  $\beta = -W$ , where  $\beta$  revolves with uniform angular velocity and  $\alpha$  oscillates along a fixed direction OQ, and is a function of the angle  $\theta$  made by  $\beta$  with the same direction, both vectors having the same origin.

The vector diagram, fig. 1 (b), indicates clearly the nature of the forces. It is to be observed that the angle  $\theta$  is measured from the positive direction of the oscillating vector.

In the expression  $P\left(\cos \theta + \frac{1}{n} \cos 2\theta\right)$ ,  $P$  and  $n$  are

\* Communicated by Dr. W. T. David, M Inst.C.E.

constants. The resulting force  $F$  is given by

$$F^2 = P^2 \left( \cos \theta + \frac{1}{n} \cos 2\theta \right)^2 - 2PW \left( \cos \theta + \frac{1}{n} \cos 2\theta \right) \cos \theta + W^2. \quad (1)$$

For simplification let  $W = kP$  and  $P = \text{unity}$ , so that  $W = k$ ,

$$\text{then } F^2 = \left( \cos \theta + \frac{1}{n} \cos 2\theta \right)^2 - 2k \cos \theta \left( \cos \theta + \frac{1}{n} \cos 2\theta \right) + k^2. \quad (2)$$

Given  $k$ ,  $F$  can be found for any angle  $\theta$ .

The particular value required in this instance is not forthcoming by treating  $F$  as a function both of  $\theta$  and the parameter  $k$ , obtaining maximum values and then solving for a minimum, or *vice versa*, by the usual methods.

Some idea of the change in the cyclical variation of  $F$  with the parameter  $k$  can be obtained from an inspection of the diagrams in fig. 1. It will be seen that as  $k$  increases

Fig. 1 (a).

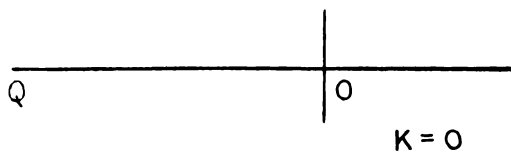
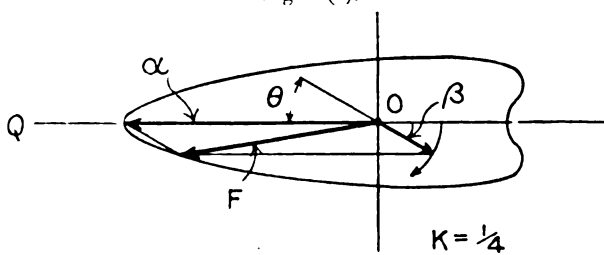


Fig. 1 (b).



from zero, fig. 1 (a), the maximum value of the radius vector  $F_{\max}$ , which at first is along the initial direction, viz.  $\theta = 0$ , becomes reduced in magnitude until, when a particular value of  $k$  is reached, three equal values of  $F_{\max}$  arise, one lying along the fixed direction whilst the other two are equally inclined to the same direction, but are on opposite sides of it, fig. 1 (d). Further increase of the parameter leads to two equal values of  $F_{\max}$ , as can be seen from an inspection of the remaining figures.

Fig. 1 (c).

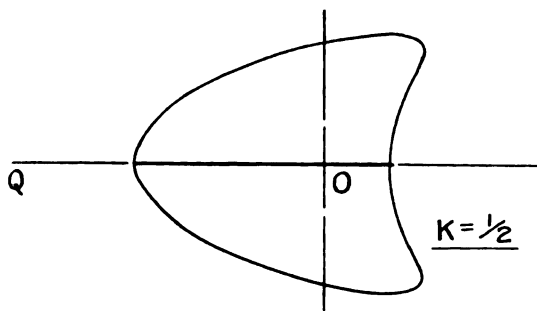


Fig. 1 (d).

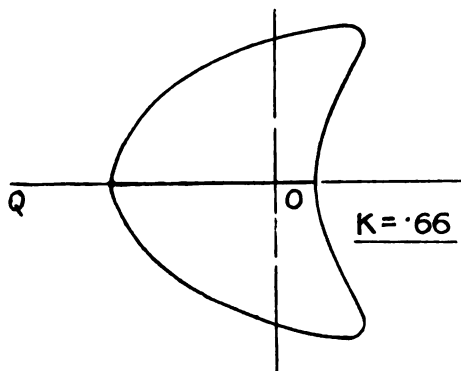
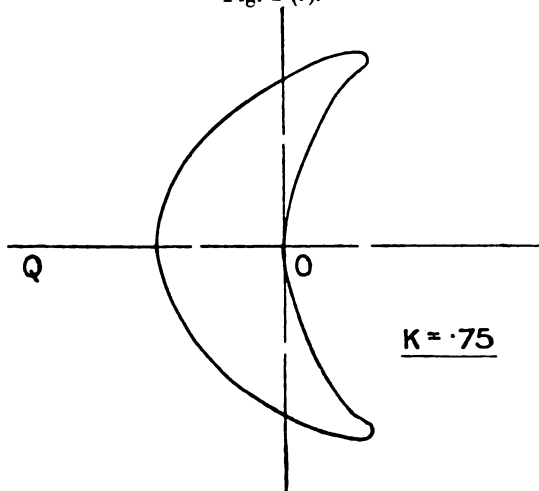
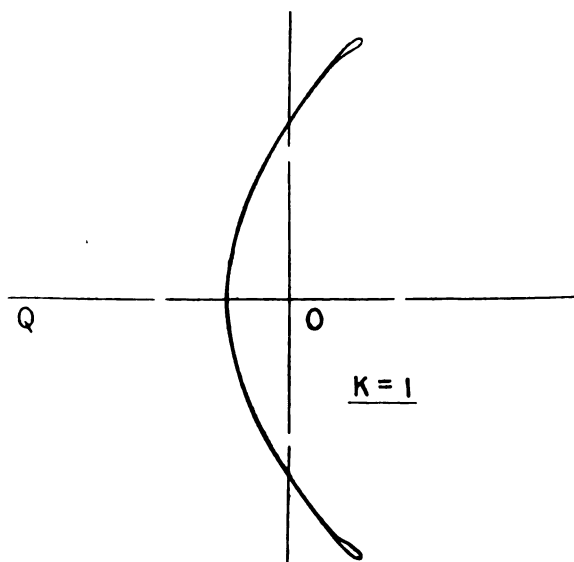


Fig. 1 (e).



In this, and similar cases, where a minimum-maximum is sought, and which cannot be evaluated by the usual methods, it is necessary to consider each case *per se* and to obtain the solution, should one exist, by particular methods. The case under consideration can be solved in the following manner,  $\pi$  being known.

Fig. 1 (f).



We have, taking  $n=4$ ,

$$F^2 = \left( \cos \theta + \frac{1}{4} \cos 2\theta \right)^2 - 2k \cos \theta \left( \cos \theta + \frac{1}{4} \cos 2\theta \right) + k^2.$$

For  $\theta=0$ ,  $F = \left( \frac{5}{4} - k \right)$ , taking the positive root. In the case when  $k$  is such that a minimum-maximum value of  $F$  results, the value of  $F$  for  $\theta=\theta_1$  (say) is the same as for  $\theta=0$ .

Let  $x = \cos \theta$ , then when the value  $F_{\theta_1}$  is equal to the value  $F_{\theta_0}$  we must have

$$\left( \frac{5}{4} - k \right)^2 = \left\{ x + \frac{1}{4} (2x^2 - 1) \right\}^2 - 2kx \left\{ x + \frac{1}{4} (2x^2 - 1) \right\} + k^2,$$

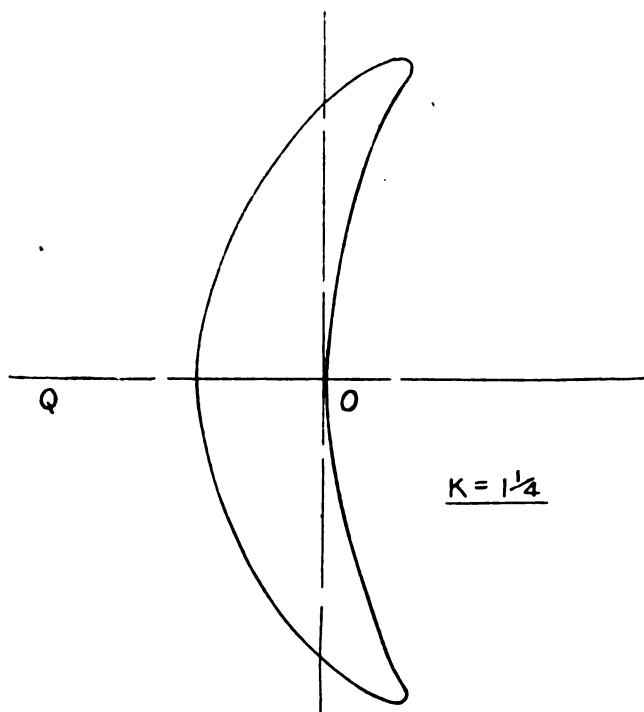
which after reduction becomes

$$\frac{3}{2} - \frac{5}{2}k = \frac{x^4}{4} + x^3(1-k) + x^2\left(\frac{3}{4} - 2k\right) + x\left(\frac{k}{2} - \frac{1}{2}\right). \quad (A)$$

We thus have one relation between  $\cos \theta$  and  $k$ .

If for a given value of  $k$  we consider the graph connecting  $F$  with  $\theta$ , at maxima and minima values, if any, we shall have  $\frac{\partial F}{\partial \theta} = 0$ , and hence another relation between  $\cos \theta$  and  $k$ .

Fig. 1 (g).



Differentiating then, equation (2) with regard to  $\theta$ , equating to zero and replacing  $\cos \theta$  by  $x$ , we have

$$2x^3 + 6x^2(1-k) + x(3-8k) + k-1=0. \quad \dots (B)$$

The equations (A) and (B) can be expressed as

$$(A) \equiv x^4 + bx^3 + cx^2 + dx + e.$$

$$(B) \equiv x^3 + fx^2 + gx + h.$$

Eliminating  $x$  we have

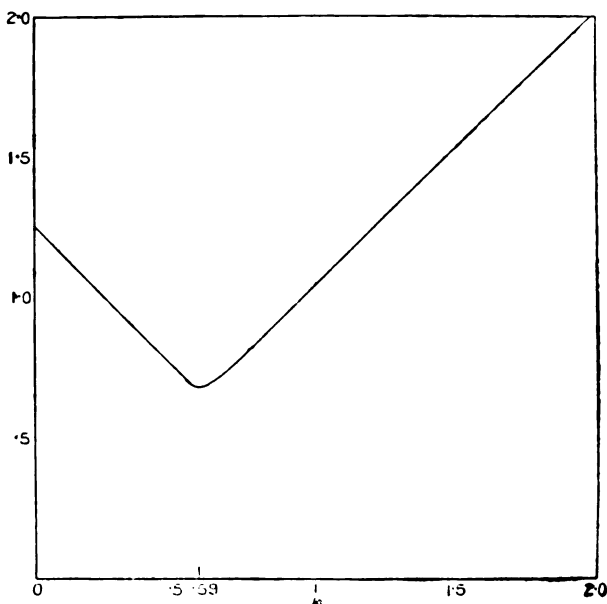
$$\begin{vmatrix} 0 & 0 & 1 & b & c & d & e \\ 0 & 1 & b & c & d & e & 0 \\ 1 & b & c & d & e & 0 & 0 \\ 0 & 0 & 0 & 1 & f & g & h \\ 0 & 0 & 1 & f & g & h & 0 \\ 0 & 1 & f & g & h & 0 & 0 \\ 1 & f & g & h & 0 & 0 & 0 \end{vmatrix} = 0.$$

Expanding the determinant and substituting for  $b, c, d$ , etc. their values in terms of  $k$  we have finally

$$676k^6 - 2561k^5 + 3299\frac{13}{16}k^4 - 2089\frac{1}{4}k^3 + 1072\frac{1}{16}k^2 - 557\frac{1}{4}k + 139\frac{3}{8} = 0, \quad (3)$$

from which  $k = .588$  very closely. This is the smallest positive root, and the only one lying between zero and

Fig. 2.



unity; hence this value of  $k$  is the one required. The equation for  $k$  may be written with the coefficients expressed

in terms of  $n$ , but in view of their complicated forms it has been thought advisable to illustrate the method by means of a numerical example.

By plotting the maxima values of the unbalanced force as determined from the diagrams of fig. 1 (together with additional values found in like manner), the curve shown in fig. 2 is obtained. This curve is almost a Vee and careful plotting is necessary in order to determine accurately the shape of the curve in the region of the vertex. The value of  $k$  determined in this manner is 0.59, which agrees closely with the value found from equation (3). The corresponding value of  $\theta$  is easily determined.

The authors hope to publish some further results in this connexion at a future date.

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LIV. *An Experimental Verification of Gibbs' Adsorption Equation by observing the Adsorption by Mercury of its own Ions from Solution, and its bearing on Nernst's Theory of Electrode Potential.* By R. KENWORTHY SCHOFIELD, B.A., Trinity College, Cambridge\*.

§ 1. *Historical.*

WARBURG<sup>(1)</sup> showed that the surface-tension of the interface between mercury and a solution of mercurous nitrate in nitric acid varies with the concentration of the mercurous salt, and concluded that the salt is adsorbed at the interface in accordance with Gibbs' adsorption equation. He sought to explain the change in surface-tension of the cathode of a capillary electrometer as the result of a change in the mercurous salt-content of the neighbouring solution due to concentration polarization. This view gained little headway against the ideas of Lippmann and Helmholtz owing to the rapidity with which the mercurous salt concentration at the cathode decreases with increasing polarizing E.M.F. Gouy<sup>(2)</sup> considered that a change in the mercurous salt-content of the solution affects the surface-tension, because it alters the electrical potential difference at the interface and, hence, the repulsive forces in the electric boundary-layer, rather than because the mercurous salts exert "capillary" forces at the interface.

Lewis<sup>(3)</sup>, and later Patrick<sup>(4)</sup>, found that mercurous sulphate is removed from aqueous solution in the neighbour-

\* Communicated by Dr. E. K. Rideal.



hood of a nozzle delivering a stream of mercury drops. They concluded that the salt is adsorbed on the surface of the drops. Neither succeeded in obtaining a quantitative measure of the amount adsorbed per unit area. Lewis considered that Gibbs' adsorption equation in its original form is not applicable to such a system, and that it is necessary to consider "electrocapillary" adsorption of the mercurous and sulphate ions in addition to "pure" adsorption of the undissociated molecules.

Euler and Hedelius<sup>(5)</sup>, more recently, have observed the decrease in concentration of an aqueous silver nitrate solution on the addition of silver foil. They favour the view of Langmuir that adsorption is due to residual valency forces operating at definitely localized places on the surface, and consider that the success of Nernst's theory of electrode potential demonstrates the chemical attraction of a metal for its own ions. They do not believe capillarity plays any part in the phenomenon, and undoubtedly there are difficulties in dealing with the surface-tension of a solid. With mercury this difficulty is removed, and Euler and Zimmerlund<sup>(6)</sup>, using a method similar to that of Lewis with the addition that its poisoning action on an enzyme was used to measure the mercurous salt concentration, have made a quantitative estimation of the adsorption of mercurous chloride by mercury, and find the amount is sufficient to quarter-saturate a unimolecular layer. No surface-tension measurements were made by which the validity of Gibbs' original equation or Lewis's modification of it might have been tested.

Gibbs<sup>(7)</sup> and Warburg (*loc. cit.*<sup>(11)</sup>) gave thermodynamic treatments of the equilibrium of an interface between mercury and dilute sulphuric acid. In this system there exists the equilibrium  $2 \text{Hg} + \text{H}_2\text{SO}_4 = \text{Hg}_2\text{SO}_4 + \text{H}_2$ ; consequently the thermodynamic potentials of only three of these substances are independently variable. Gibbs regarded the potential of  $\text{Hg}_2\text{SO}_4$  as dependent on the rest, while Warburg so regarded the potential of  $\text{H}_2$ ; consequently their conclusions, though both thermodynamically correct, differ in form. The thermodynamic potentials of the ions  $\text{Hg}_2^{++}$ ,  $\text{SO}_4^{--}$ ,  $\text{H}^+$ ,  $\text{OH}^+$ , and electrons may all be regarded as independently variable subject to the restriction that there can be no volume charge. The ambiguity of the former treatment disappears, but care has to be taken in relating the potentials to composition and electrical potential of the phases. Van Laar<sup>(8)</sup> and Frumkin<sup>(9)</sup> have attempted to

use these variables, but the author does not consider either treatment completely satisfactory.

Nernst<sup>(10)</sup> attempted to relate his theory of electrode potential to electrocapillarity, but failed to effect a satisfactory union owing to the erroneous idea, current during the closing years of last century, that a mercury electrode showing its maximum surface-tension is necessarily at the same electrical potential as the electrolyte with which it is in contact. This notion has been proved incorrect by the work by Gouy<sup>(11)</sup>, Smith<sup>(12)</sup>, and others, but no attempt has been made to remodel Nernst's theory in the light of this fact.

In § 2 of the present paper an attempt is made to give as concisely as possible the result of applying the thermodynamic methods of Gibbs, and the principles of electrostatics to the equilibrium of an interface between a metal and an electrolyte containing its ions. Part of it is original, but where possible use is made of those parts of existing treatments which appear correct. In this way Nernst's theory, in a form which does not involve the physical existence of an "ionic solution pressure," or the fallacy referred to above, Helmholtz' original theory of the electric *boundary* layer (as distinct from the subsequent particular theory of the *double* layer), Lippmann's equation, and Gibbs' adsorption equation are all inter-related. In § 3 experiments designed to test a conclusion arrived at in § 2 are described. The results besides confirming this are seen in § 4 to support Warburg's original idea, and the views of Gouy, of Lewis, and of Euler and Hagedius are there discussed.

## § 2. Theoretical.

According to Gibbs<sup>(1)</sup> any constituent of a system in equilibrium must have the same thermodynamic potential in all the phases of which it is a component. Hence when equilibrium has been established across an interface between a metal and an electrolyte containing its ions, the thermodynamic potential  $\mu_{\text{Me ions}}$  of the metallic ions must be the same in both. In general the thermodynamic potential of a constituent which is electrically neutral may be said to depend only on its concentration  $C$  and its "environment," but if it is an ion, the electrical potential of the phase must also be considered. In the present system, if the electrical potential of the electrolyte be reckoned as zero and that of the metal  $\Delta$  (in volts), the thermodynamic potential of the

metallic ions in ergs per gr. ion will be

$$\left. \begin{aligned} \mu_{\text{Me ions}} &= RT \log_e C + k_e \text{ for the electrolyte} \\ &= 96.5 \times 10^{10} n \Delta + k_m \text{ for the metal} \end{aligned} \right\}, \quad (\text{i.})$$

where  $k_e$  represents the "environment" in the electrolyte, and is only independent of  $C$  when the latter is small,  $96.5 \times 10^{10} n$  is the charge on a gr. ion in coulombs  $\times 10^{-7}$ ,  $n$  is the valency of the metallic ions, and  $k_m$  embraces both the concentration and "environment" in the metal and is evidently independent of  $\Delta$ . Hence

$$\Delta = \frac{1}{96.5 \times 10^{10} n} \left\{ RT \log_e C - (k_m - k_e) \right\} \quad (\text{ii.})$$

In this relation  $k_m - k_e$  is proportional to the logarithm of Nernst's "ionic solution pressure" <sup>(14)</sup>, but is seen to depend on the properties of the electrolyte as well as on those of the metal\*.

Were it supposed that at an interface the density of each component changed abruptly at an imaginary geometrical surface, being constant on either side into the interior of each phase, the amount of each component actually present in the system would differ from that calculated on this basis by an amount depending on the position chosen for this dividing surface <sup>(15)</sup>. By a suitable choice, however, the surface excess of any one component can be made to vanish, and in the present system it is convenient to so choose it that there is no surface excess or deficit of metallic ions at the interface, since these are the one constituent present in both phases. In accordance with this convention all the metallic ions in the system are assigned to one or other of the bulk phases.

If at the instant when the metal comes into contact with the electrolyte it is not at the electrical potential necessary for equilibrium, the thermodynamic potential of the metallic ions in the two phases will differ, and consequently some of them will pass from the phase in which their potential is higher to that in which it is lower. This phenomenon may conveniently be called the "Nernst ionic transfer."

\* Butler (Trans. Faraday Soc. xix. p. 729 (1924)), and Heyrovsky (Proc. Roy. Soc. A, cii. p. 627 (1923)), have given expressions relating  $\Delta$  to the molecular properties of the metal and the electrolytes. Their treatments may be regarded as attempts to evaluate  $k_m$  and  $k_e$  in terms of the ionization potential of the metal and the heat of hydration of the ions in the solvent.

From electrostatic principles Helmholtz<sup>(16)</sup> derived the expression

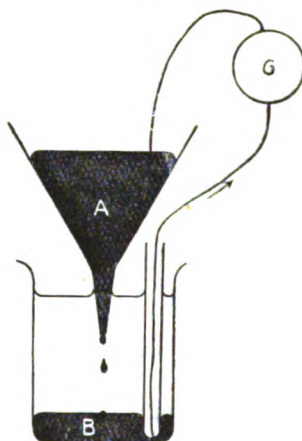
$$\Delta = 4\pi M \times 300, \quad . \quad . \quad . \quad . \quad . \quad (iii.)$$

where  $M$  is the electric moment of the interface in E.S.U. per sq. cm. Hence two phases in contact can only be at a difference of electrical potential  $\Delta$  when the electrical distribution in the interfacial layer gives rise to the necessary moment. Thus, although the equilibrium value of  $\Delta$  is determined solely by the chemical composition of the two homogeneous phases, a particular molecular and ionic arrangement must be established in the intervening non-homogeneous layer in order that the conditions of chemical and electrical equilibrium may be simultaneously obeyed. An addition of ions to the metallic phase by means of a "Nernst ionic transfer" will give rise to a surface deficiency of electrons (the other component of the phase); similarly, their removal will cause a surface excess of electrons. Since there can be no net volume charge the surface density of the other ions of the electrolyte with respect to the dividing surface must always have a charge equal and opposite to that of the surface density of electrons. The resulting distribution will give rise to an electric moment the value of which, for bulk phase of given composition, will depend only on the surface density of electrons. The exact relation between these two quantities cannot be deduced from general principles unaided by specific molecular hypotheses. In spite of this it is evident that the "Nernst ionic transfer" will continue until the resulting surface density of electrons is sufficient to set up the moment necessary to give the value of  $\Delta$  required for the equilibrium of the metallic ions.

If the metal be a liquid, such as mercury, and the interface at which equilibrium has already been established be expanded, a "Nernst ionic transfer" will occur in order to establish at the new surface the necessary surface density of electrons, but it is evidently immaterial whether the transfer occurs at the newly-made surface or on the old. In particular, if the metallic phase be in two parts A and B connected by a wire, and the surface of A be enlarged, equilibrium can be established by a transfer at the surface of B and the passage of an equivalent electric charge along the connecting wire. Moreover, if the surface of A expands at the same rate as that of B is contracting, there will be no change in the total area of the interface, and consequently equilibrium can be maintained simply by a movement of

electrons from one part of the phase to the other, *i. e.*, simply by the passage of a current along the connecting wire, a process by which equilibrium is set up far more rapidly than by the diffusion of ions. Such a system is shown in fig. 1, an arrangement described by Varley<sup>(16)</sup> and later by Lippmann<sup>(17)</sup>. If dilute sulphuric acid be the electrolyte, it will attack the mercury if it contains dissolved oxygen.

Fig. 1.



Consequently mercurous sulphate will be present in solution at an appreciable concentration. Under these circumstances the direction of the current which flows through the galvanometer as the drops fall shows that there is a deficit of electrons at the interface at equilibrium\*.

Lippmann related the surface electrification, of which these experiments give evidence, to the rate of change of the surface tension  $\sigma$  of the interface (in dynes/cm.) with  $\Delta$ . His method of deducing this relation has been criticized, but the result is undoubtedly correct, and can be obtained by an application of Gibbs' <sup>(18)</sup> adsorption equation (at constant temperature)

$$d\sigma = -\Sigma \Gamma d\mu,$$

in which the summation extends over all the *independently variable* components of the system. We may regard these

\* An arrangement described by C. T. R. Wilson (Proc. Roy. Soc. A, xcii. p. 505 (1916)) and used by him to measure the passage of charges works on this principle, and depends for its action on the fact that the acid creeps between the mercury and the glass.

as  $\text{Hg}_2''$ ,  $\text{SO}_4''$ ,  $\text{H}'$ ,  $\text{OH}'$ , and electrons, since all the constituents present can be regarded as composed of two or more of these. If a change of  $\sigma$  with  $\Delta$  be considered in which the strength of the sulphuric acid remains unaltered,  $d\mu$  for  $\text{SO}_4'$ ,  $\text{H}'$ , and  $\text{OH}'$  is zero,  $\Gamma$  for  $\text{Hg}_2''$  is also zero on account of the choice of dividing surface, and only the term relating to the electrons remains.  $d\mu$  for the latter is evidently  $96.5 \times 10^{10} d\Delta$ . Hence

$$\Gamma_{\text{electrons}} = \frac{1}{96.5 \times 10^{10}} \frac{d\sigma}{d\Delta}, \quad . \quad . \quad . \quad (\text{iv.})$$

$\Gamma_{\text{electrons}}$  being measured in gr. equivalents per sq. cm. If  $\Gamma_{\text{electrons}}$  be replaced by its equivalent electric charge,  $\epsilon$ , in coulombs per sq. cm., we obtain Lippmann's equation

$$\frac{d\sigma}{d\Delta} = \epsilon \times 10^7. \quad . \quad . \quad . \quad . \quad . \quad (\text{v.})$$

Lippmann measured  $d\sigma/d\Delta$  with a "capillary electrometer," a cell of which the cathode is a mercury thread in a capillary tube, so arranged that the surface-tension of the interface can be measured. An E.M.F.,  $V$ , is applied between this cathode and a mercury anode presenting a large surface to the electrolyte. If the latter is rendered "unpolarizable" by covering it with crystals of the appropriate mercury salt,  $\Delta$  remains unaltered at the anode and  $d\Delta$  at the cathode  $= -dV$ . Hence  $d\sigma/d\Delta = -d\sigma/dV$ . The  $\sigma - V$ , or electrocapillary, curve for sulphuric acid of a strength used by Lippmann is nearly (but as the most recent measurements show, not exactly) parabolic,  $\sigma$  rising to a well-defined maximum value. For other electrolytes, notably KI, the curve is not even approximately parabolic. Guided by Lippmann's measurements on sulphuric acid, Helmholtz<sup>(19)</sup> attempted to relate  $\epsilon$  to  $\Delta$  by means of equation (iii.) by assuming the moment of the interface to be due to a double layer consisting of a charge  $\epsilon$  on the mercury and a complementary layer of oppositely charged ions at a small distance. The work of Gouy<sup>(11)</sup>, Smith<sup>(12)</sup>, and others has shown that the electrical distribution cannot in general be so simple. In particular  $\Delta$  is not always zero when  $\epsilon$  is zero, a fact fatal to the simple Helmholtz theory. The breakdown of the simple double-layer theory does not, however, affect the validity of Lippmann's equation, of which Frumkin<sup>(20)</sup> has recently obtained experimental confirmation, both by showing that an insulated dropping always takes up the

potential of the maximum of the electrocapillary curve \* and also by measuring  $\epsilon$  quantitatively with an apparatus similar to that of fig. 1, and comparing the values of  $\epsilon$  thus obtained with those of  $d\sigma/dV$  found with a capillary electrometer in the neighbourhood of  $V=0$ . Frumkin used, besides sulphuric acid, solutions for which the electrocapillary curve is far from parabolic and for which the electric boundary layer is undoubtedly complex. Assuming the general validity of Lippmann's equation  $d\Delta/de$  is found to be always positive, a condition necessary for the establishment of electrical equilibrium by the "Nernst ionic transfer."

It thus appears that the surface concentration calculated as above with the aid of Gibbs' adsorption equation is equal on the one hand to minus the surface charge found by Lippmann's equation from the slope of the electrocapillary curve and expressed in gr. equivalents per sq. cm., and on the other hand to minus the number of gr. equivalents of mercurous ions taken up by an expanding mercury surface or thrown off a contracting one per unit area in course of the "Nernst ionic transfer."

### § 3. *Experimental.*

In order to test this conclusion experimentally, measurements were made on a modified form of Patrick's "constant flow" adsorption tube (*loc. cit.* <sup>(4)</sup>). A quantity of dilute sulphuric acid containing mercurous sulphate was rendered oxygen-free by boiling, and stored in a flask in an atmosphere of nitrogen. When cold this solution was driven under nitrogen pressure from an aspirator along a delivery tube and entered the adsorption tube at A (fig. 2).

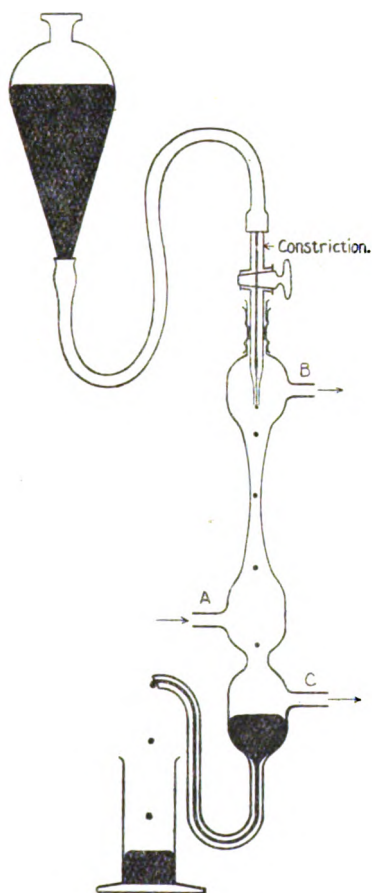
Instead of all passing upwards past the tip from which the mercury drops fell, as in Patrick's experiments, the stream divided, part travelled downwards over the mercury surface into which the drops coalesced at the lower end of the adsorption tube. In this way it was possible to measure the amount of salt adsorbed by the drops in their formation, and also the amount given back to the solution when they disappeared.

The arrangement shown in fig. 3 was used to find the change in concentration of the mercurous ions produced by the falling drops. Preliminary experiments showed that when a stream of the above solution is sent through this apparatus the potential difference between the mercury

\* An observation originally due to Paschen (Wied. Ann. xli. p. 42 (1890)); cf. also Smith and Moss (Phil. Mag. (6) xv. p. 428 (1908)).

covered with solid  $\text{Hg}_2\text{SO}_4$  in D and that in contact with the stream in the cup E depends on the speed of the stream as well as on its mercurous salt-content. With the cup E made in a capillary tube, as shown, it was found, however, that this potential difference is constant when the flow-rate

Fig. 2.

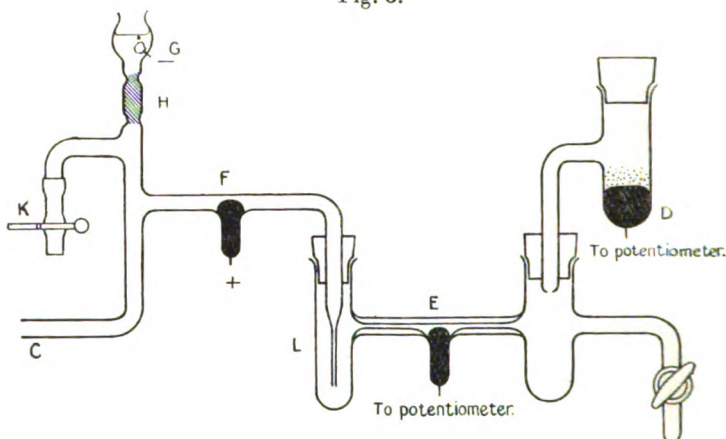


exceeds a critical value. The cause of this effect was never satisfactorily traced, but as will be apparent it did not affect the validity of the final results. Mercurous sulphate could be added to the stream before it reached E by passing a current between the mercury cup F (as anode) and the



platinum foil G, from which hydrogen bubbled. The connecting-tube H was filled with 2 per cent. agar-agar jelly, and had two constrictions to prevent the pressure from dislodging it. By means of the side-tube K, the tube joining the agar-tube to the rest of the apparatus could be washed out from time to time, thus preventing any products of the jelly from diffusing into the main stream. In order to overcome the difficulty of mixing the layer of concentrated solution, which was carried away from F uniformly with the rest of the solution, the arrangement shown at L

Fig. 3.



was finally adopted. It was found that with a sufficiently rapid flow-rate the change in the potential difference between D and E was proportional to the current sent between F and G, and inversely proportional to the flow-rate. This was considered a satisfactory indication that the apparatus was reliable.

With the solution leaving the adsorption tube at both B and C (fig. 2) at a rate sufficient for the satisfactory working of "electrolytic injectors" (as the arrangements in fig. 3 may conveniently be called) attached at these points, no mixing occurs between the liquid which flows over the lower mercury surface and that which passes the dropping tip. A quantitative measure of the rate at which mercurous ions are thrown off the drops as they coalesce can therefore be made as follows. A steady flow in at A and out at B and C is set up, and mercury is set dropping from the tip at a uniform rate (siphoning out at the bottom). The solution

entering an electrolytic injector attached at C thus contains the mercurous ions thrown off, the drops in addition to those originally in the solution entering at A. When the potential difference between D and E has become steady it is balanced with a potentiometer, using a sensitive galvanometer. On turning off the mercury drops the solution leaving the adsorption-tube at C is the same as that entering at A, and the potentiometer is consequently thrown out of balance. Without touching the potentiometer the galvanometer can be brought back to zero by passing a current, suitably adjusted by a rheostat, between F and G. It is evident that a measurement of this current enables the number of gr. equivalents of mercurous ions liberated per second by the coalescence of the drops to be calculated, since the rate of liberation of ions by the electrode F must have been exactly equal to this. An "electrolytic injector" attached at B permits of a measurement of the rate at which mercurous ions are removed from the upper stream when the mercury drops are falling, by finding the compensating current necessary to restore a potentiometer balance obtained before the drops were turned on.

Since a minimum flow-rate is necessary for a satisfactory working of the "electrolytic injector," only small changes in the concentration are effected, and it is necessary to have a drop-rate faster than can be counted with the unaided eye if accurate results are to be obtained. The drops were therefore counted with the aid of a rotating stroboscopic disk mounted on a Rayleigh-Wilberforce synchronous motor. The current interrupter used was so constructed that the effective length of the trembler could be varied while the motor was running. In this way the disk could not only be kept rotating at a uniform speed, but also the speed could be altered at will. Using a dropping tube with a constriction in it and a large head of mercury, steady dropping could be obtained up to 30 drops per second, further increase in the head produced a jet. With the aid of a fine adjustment on the height of a reservoir, the drop rate could be kept constant to two per cent. The mercury siphoned steadily out of the bottom of the adsorption-tube without giving rise to any noticeable fluctuations in the level of the mercury. A bell on the synchronous motor rang for every 3000 drops, that is for every hundred turns of the stroboscopic disk which had thirty slits. By weighing the amount of mercury collected between successive rings of the bell, the weight and hence the area of a drop could be found. By finding the time interval between successive

rings the adsorbing area formed at the tip and removed at the bottom per second can be calculated.

Measurements on the stream emerging at C showed that, with solutions of the same composition, the rate of production of mercurous ions is independent of the flow-rate and proportional to the rate of disappearance of drop-surface. The ions simultaneously removed from the other stream by the equally rapid formation of drop-surface at the tip was always less than those given to the lower stream, and the discrepancy was greater the faster the drop-rate and the slower the flow-rate. It became evident that whereas a still mercury surface is not attacked by oxygen-free sulphuric acid, since a drop of mercury placed in the flask containing the solution \* caused no measurable increase in the mercurous ion concentration when left undisturbed for several weeks, a rapidly expanding surface is so attacked. It was found that shaking the flask, and thus causing the drop-surface to expand and contract successively, increased the mercurous ion concentration. More shaking always produced more mercurous ions, proving the effect was not due to the formation on standing of a concentrated layer near the still drop, which shaking mixed with the rest of the solution. The action of sulphuric acid on an expanding mercury surface has already been studied by Smith<sup>(21)</sup>, who has in certain cases observed the evolution of hydrogen. The effect was lessened by replacing some of the sulphuric acid by sodium sulphate, but even with a solution  $\frac{3}{40}n\text{Na}_2\text{SO}_4 + \frac{1}{40}n\text{H}_2\text{SO}_4$  used in the final measurements there still exists the irreversible production of mercurous ions as the drops are formed. It was not found satisfactory to use a neutral sodium sulphate solution owing to the formation of basic mercurous sulphate, which is not sufficiently soluble.

The final measurements were confined to the lower stream, and the measurements by which the number of gr. equivalents of mercurous ions given to the solution on the disappearance of unit area of drop-surface were calculated are summarized in Table I. for the three strongest solutions used. The measurements necessary are those of a current, a weight and a time in each case. All these can be found to at least one per cent. The reliability of these depend on the accuracy to which the drop-rate was synchronized with the stroboscope and the accuracy to which the potentiometer balance could be observed. The latter was the greater uncertainty as the

\* To reduce any mercuric ions that might initially be present.

TABLE I.

E.M.F. in millivolts.	Galvanometer (double) deflection.	Gr. equivs. liberated per sec. $\times 10^{-10}$ .	Time for 3000 drops in secs.	Weight of 3000 drops in grs.	Area of 3000 drops in sq. cms.	Nernst ionic transfer in gr. equivs. per sq. cm. $\times 10^{10}$ .	Ccs. of solution per minute.
18.0	29.0	5.08	125	43.9	152.5	4.16	9.1
"	28.0	4.82	135	44.4	153.8	4.23	17.5
"	25.0	4.40	177	52.2	172.2	4.53	11.4
"	22.5	3.96	180	53.4	173.8	4.09	19.0
							4.23
30.5	20.2	3.54	198	57.2	182.1	3.85	7.3
"	19.5	3.41	198	56.9	181.1	3.72	12.9
"	22.8	3.99	148	49.6	165.5	3.57	12.8
"	21.5	3.77	174	57.3	182.3	3.61	20.5
							3.69
42.0	16.0	2.80	188	57.2	182.1	2.89	12.3
"	21.0	2.32	175	53.5	174.1	3.34	14.7
"	18.0	3.15	172	55.3	178.0	3.04	18.4
"	17.3	3.07	184	56.7	181.0	3.12	19.0
"	16.7	2.86	194	56.1	179.7	3.09	19.5
							3.10

lack of balance to be corrected by the compensating current amounted to a few millivolts only, and this entirely accounts for the differences between successive observations on the same solution. The E.M.F. in the first column is a measure of the concentration of the solution.

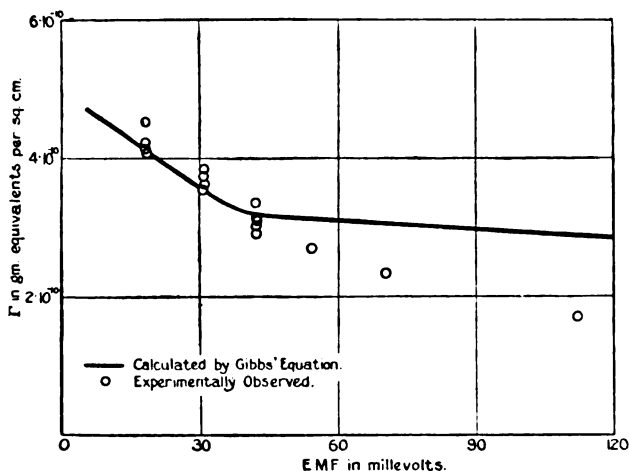
To obtain the values of  $\Gamma_{\text{electron}}$  given by Gibbs' adsorption equation, a capillary electrometer similar to that used by Smith (*loc. cit.* <sup>(12)</sup>) was set up. The anodic mercury was covered with mercurous sulphate, and the same solution,  $\frac{3}{4}n\text{Na}_2\text{SO}_4 + \frac{1}{4}n\text{H}_2\text{SO}_4$ , was used as in the previous experiments. The distance from the capillary meniscus to the top of the column at the maximum of the electrocapillary curve was 25.2 cm. Gouy's <sup>(22)</sup> value for the maximum surface-tension is 427 dynes/m., hence 1 cm. of mercury corresponded to  $427/25.2 = 16.9$  dynes/cm. The changes in surface-tension between  $V=0$  and  $V=0.12$  were accurately determined by applying air-pressure, recorded on a water-manometer, to the top of the mercury column of which the height was not altered. The applied E.M.F. and water-manometer readings are given in the first and second columns of Table II. over a sufficient range for comparison to be made with Table I. One centimetre of water corresponds to  $16.9/13.56 = 1.25$  dynes/cm. The change of surface-tension between 10 and 20 millivolts is  $3.3 \times 1.25 = 4.12$  dynes/cm. By equation (iii.)  $\Gamma_{\text{electrons}} = \frac{4.12}{0.01} \times \frac{1}{9.65 \times 10^{10}} = 4.27 \times 10^{-10}$ . The other values in column four were similarly calculated.

TABLE II.

E.M.F. in millivolts.	Difference in level of water- manometer in cm.	Difference.	$\Gamma_{\text{electrons}}$ in gr. equivalents per sq. cm. $\times 10^{-10}$ .
10	3.2	...	...
15	4.9	3.3	-4.27
20	6.5	3.1	-4.01
25	8.0	2.9	-3.75
30	9.5	2.8	-3.62
35	10.8	2.6	-3.37
40	12.1	2.5	-3.24
45	13.3	2.5	-3.24
50	14.6	...	...

From fig. 4 it will be seen that the agreement for the solutions richer in mercurous sulphate (small E.M.F.'s) between the value of  $\Gamma_{\text{electrons}}$ , calculated with the aid of Gibbs' adsorption equation (or Lippmann's equation) and the "Nernst ionic transfer," directly observed at a contracting interface leaves nothing to be desired. The values for more dilute solutions (not given in the tables) show a discrepancy, increasing with the E.M.F., and probably due to the rate of diffusion of mercurous ions being insufficient to bring the tops to equilibrium before entering the downward flowing stream. Since the concentration of mercurous ions

Fig. 4.



decreases ten-fold for each 29 millivolts, we should expect the observed adsorption to fall off very rapidly with increasing E.M.F. were the ions discharged into the lower stream equal to those which diffused up to and were deposited upon the drop during its formation and fall in the upper stream. The fact that when the concentration is just too small to effect equilibrium, the subsequent decrease in the amount removed does not approach ten-fold with an increase of 29 millivolts in the E.M.F., is additional proof that the surface concentration of electrons set up at an expanding mercury surface is not entirely due to mercurous ions diffusing up to the surface, but is in part due to the production of mercurous ions by the chemical action of the acid on the expanding surface.

If this explanation for the discrepancy at the larger E.M.F.'s be accepted these experiments, besides giving a quantitative measure of the "Nernst ionic transfer," constitute an exact quantitative verification of an expression derived by the application of Gibbs' adsorption equation\* by confirming the conclusions of the last section.

#### § 4. *Conclusion.*

These experiments may alternatively be taken as affording a measure of the quantity of mercurous sulphate which must be removed from a solution in contact with mercury when the interface contracts by unit area in order to maintain the mercurous sulphate concentration in the solution unaltered†, and as thus confirming the conclusion derived by Warburg from Gibbs' adsorption equation that this is the electrochemical equivalent of  $e$  of Lippmann's equation. It has already been observed that a surface charge can be formed by the retreat of electrons from the surface, but it is evident that this process can alternatively be regarded as a flux of electricity across the interface, which produces an equivalent quantity of mercurous sulphate in accordance with Faraday's laws. It must therefore be concluded that on increasing the area either a flux of electricity must pass across the interface, or an equivalent amount of mercurous sulphate must diffuse up to it from the solution (or be produced there by chemical action) in order to bring about equilibrium between the phases. In the experiments of Frumkin and those described above, the attainment of equilibrium by these two methods is studied, and they confirm quantitatively the conclusions obtained by applying Gibbs' adsorption equation. Neither these experiments nor the equation of Gibbs, however, give any clue as to why, from the standpoint of molecular mechanics, the presence of excess mercury salt at the interface is necessary for its equilibrium, nor yet as to the nature of the forces which hold it to the surface. They give no information as to the state of combination or dissociation of the mercurous sulphate when it has reached the interface, or its arrangement. Though its presence has evidently an influence

\* Up to the present time the most exact verification of Gibbs' adsorption equation has been obtained by Donnan and Barker (Proc. Roy. Soc. A, lxxxv. p. 557 (1911)) for the adsorption of nonylic acid at a water-air interface. Discrepancies of the order of 50 per cent. were observed.

† In order to maintain a net zero charge in the system a number of sulphate ions equivalent to the number of mercurous ions must be simultaneously removed.

both on the electric moment of the interface, and on the surface-tension, no information can be obtained in this way about the precise molecular mechanisms at work \*.

It is therefore apparent that the view of Euler that the adsorbed substance is held to the surface in the manner conceived of by Langmuir, that of Lewis that both ions and undissociated molecules are present at the interface, and that of Gouy that the surface-tension is affected by electrical repulsive forces in the Helmholtz boundary-layer, have no bearing on the question of the validity of Gibbs's adsorption equation. Any of these ideas may in the future be proved correct, partly correct, or incorrect, but in no case will the basis of the Gibbs equation be affected. The information which can be obtained by the use of Gibbs's method is strictly limited, but such as it is, it is entirely independent of questions of mechanism.

#### *Summary.*

1. Direct experimental measurements show that the amount of mercurous sulphate adsorbed at a mercury surface in contact with an electrolyte containing this salt corresponds quantitatively with that calculated from surface-tension measurements by Gibbs' adsorption equation.

2. The number of mercurous ions adsorbed at a freshly expanded interface is identified with the number of ions which on the Nernst theory of electrode potential are deposited on the mercury surface, and impart to it their charge.

3. This surface charge is equal to that calculated from the slope of the electrocapillary curve with the aid of Lippmann's equation, and regarded as a surface deficit of electrons may also be evaluated by a direct application of Gibbs' adsorption equation.

4. The surface charge may be set up by a retreat of

\* Such information can only be obtained by inductive methods applied to the relation experimentally founded between the surface-tension, surface concentration, and other properties of the interface. It has been shown (Schofield and Rideal, *Proc. Roy. Soc. A*, cix. p. 57 (1925)) that in some cases surface films lower the surface-tension solely in virtue of their kinetic agitation. An accurately parabolic electrocapillary curve could be interpreted by supposing the adsorbed molecules each to have the same electric moment perpendicular to the interface, and to repel one another with a force varying inversely as the fourth power of their distance apart. It is hoped to take up this matter in more detail in the near future.



electrons from the surface, *i. e.*, by a flux of electricity across the interface.

5. This flux may in turn be regarded as producing at the surface, in accordance with Faraday's laws, the same quantity of mercurous sulphate as would be adsorbed from solution had no electric flux taken place.

In conclusion, I gladly take this opportunity of expressing my thanks to Dr. Rideal for constant help and advice during the progress of this work, and to the Board of Scientific and Industrial Research for a grant.

### References.

- (1) Warburg, *Wied. Ann.* (9) xli. p. 1 (1890).
- (2) Gouy, *Annales* (7) xxix. p. 149 (1903).
- (3) Lewis, *Zeit. Phys. Chem.* lxxvii. p. 129 (1910).
- (4) Patrick, *Zeit. Phys. Chem.* lxxxvi. p. 545 (1914).
- (5) Euler and Hedelius, *Arkiv. Kemi. Min. Geol.* vii. No. 31 (1920).
- (6) Euler and Zimmerlund, *Arkiv. Kemi. Min. Geol.* viii. No. 14 (1921-1922).
- (7) Gibbs, *Collected Papers*, i. pp. 335 and 336.
- (8) Van Laar, *Zeit. Phys. Chem.* xli. p. 385 (1902).
- (9) Frumkin, *Zeit. Phys. Chem.* ciii. p. 56 (1922).
- (10) Nernst, *Zeit. Phys. Chem.* iv. p. 129 (1889).
- (11) Gouy, *C. R.* cxxxi. p. 939 (1900) and *Annales de Physique* (9) vii. p. 129 (1917).
- (12) Smith, *Phil. Trans. A*, cxciii. p. 70 (1900).
- (13) Gibbs, *loc. cit.* (7) p. 65.
- (14) Nernst, *Zeit. Phys. Chem.* ii. p. 163 (1889).
- (15) Varley, *Phil. Trans. A*, ci. p. 29 (1871).
- (16) Helmholtz, *Wied. Ann.* vii. p. 337 (1879), *Physical Memoirs*, 1888.
- (17) Lippmann, *C. R.* lxxvi. p. 1407 (1875); *Pogg. Ann.* cxlix. p. 561 (1873); *Annales*, v. p. 494 (1875).
- (18) Gibbs, *loc. cit.* p. 230, equation 508.
- (19) Helmholtz, *Monats. Konig. Preuss. Akad. Wiss. Berlin*, 1881, p. 947.
- (20) Frumkin, *loc. cit.* (9).
- (21) Gouy, *Annales de Physique*, vi. p. 5 (1916).
- (22) Smith, *Phil. Mag.* (6) xvii. p. 833 (1909).

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Cambridge.  
Nov. 21st, 1925.

LV. *Adsorption of Carbon Dioxide by Activated Coconut Charcoal.* By H. ROWE, B.Sc., *Demonstrator in Physics, University College of the South-West of England, Exeter* \*.

1. *Introduction.*

**A**DSORPTION with charcoal at low pressures must depend on the specific attraction of the solid for the gas molecules, and also upon the extent of the solid surface exposed to the gas, the attraction between the gas molecules being altogether negligible in comparison with that between the gas and the solid.

As the pressure is increased, the packing of the gas molecules upon the surface will become tighter, and a stage will be reached at which the gas molecules can accumulate further only by adhering to others already anchored. Then the mutual molecular attraction will become a factor of importance, and eventually, as the pressure becomes such as to bring the outside gas near to liquefaction, the adsorption of gas molecules will proceed at an intensified rate, filling the capillaries in the order of their fineness,

The largest capillaries of charcoal can be seen under the microscope, and, on an average, are  $10^{-2}$  mm. in diameter †, or about 13,000 times the diameter of a nitrogen or hydrogen molecule. Lamb, Wilson and Chaney ‡ estimated the average diameter of the pores of activated charcoal, including the finest with the coarsest openings, to be about  $5 \times 10^{-6}$  mm., which is less than 7 times the diameter of the gas molecule. Lowry and Hulet § calculated the mean diameter of the capillaries, and found it varied between  $2.8 \times 10^{-6}$  mm. and  $9.2 \times 10^{-6}$  mm., the surfaces of the various charcoals ranging from 160 sq. metres to 436 sq. metres per gram of charcoal. It may be inferred from these figures that the greater part of the internal gaseous space of an efficient adsorbent consists of passages that are not much larger than the gas molecule.

In order to explain the phenomenon of adsorption several theories have been suggested, some of which will now be briefly considered.

1. *Chemical combination.* A theory of chemical combination has been brought forward in order to account

\* Communicated by Prof. F. H. Newman, D.Sc., A.R.C.S.

† See H. Briggs, *Proc. Roy. Soc. A.* vol. c. p. 88 (1921).

‡ *Journ. Indust. Eng. Chem.* xi. p. 420 (1919).

§ *Journ. Amer. Chem. Soc.* xlii. p. 1408 (1920).

for the large amount of heat generated during the adsorption process.

2. Solid solution. This theory, accepted by Miss Homfray \* as being the most consistent with her results, contemplates the actual penetration of the gas into the charcoal, the concentration being constant throughout the mass of the charcoal.

3. Solid condensation. This third theory—which accounts for the large amounts of gas adsorbed with a small quantity of charcoal better than the two theories given above—assumes that the gas is condensed upon the charcoal surface. This theory resulted from the fact that in early experiments the easily liquefied gases were always adsorbed to a great extent, and the investigators were led to believe that the adsorbed gas was condensed by the charcoal.

McBain †, as a result of his experiments with hydrogen and charcoal, considers that two processes occur. A condensation of gas on the charcoal surface is completed within two or three minutes, and a solid solution is formed by a slow diffusion—which may take more than 24 hours for completion—into the interior of the charcoal.

Langmuir ‡ has suggested a theory which in many respects is an elaboration of the solid solution and solid condensation theories. According to his theory, a gas molecule approaching a solid surface comes into the field of force of the atoms of the solid, and in general these gas molecules condense on the surface no matter what the temperature may be. At the same time, evaporation, the rate of which depends on the temperature, comes into play. Adsorption is a direct consequence of a time lag between condensation and subsequent evaporation. The adsorbed layer, according to Langmuir, does not exceed one molecule or, at the most, a few molecules in thickness. In order to account for the large volume of gas adsorbed by charcoal and other substances, he assumes that such substances present a much greater surface area than is apparent.

When plotting the relation between equilibrium pressure and gas adsorbed the resulting curve is always continuous, and is characteristic of a continuous series of solid solutions. No definite compound is formed and, usually, equilibrium is reached fairly rapidly—an argument, although by no means a conclusive one, against the existence of a solid solution.

\* *Zeits. Phys. Chem.* lxxiv. p. 129 (1910).

† *Phil. Mag.* xviii. p. 916 (1909).

‡ *Phys. Rev.* viii. p. 149 (1916).

While the experiments on gaseous adsorption by charcoal show conclusively that the surface phenomena are important, there is also the possibility that a solid solution may be formed.

In the majority of cases the intermingling phenomena that constitute sorption have not been disentangled or even experimentally identified. From a theoretical point of view true adsorption, *i. e.* surface condensation, or the difference in concentration of the gas at the surface and within the bulk of the gas, attracts by far the most attention. Yet the phenomena of absorption or true solution in a solid are also of interest, and frequently the chemical reactions that ensue are of decisive importance, as for example in the case of catalysts.

It is important to insist on the distinction between the different factors because time relationships of adsorption and of absorption and again of chemical reaction are found to be widely different. The laws governing the amounts of gas sorbed by these processes also differ, but this is of less importance because when adsorption is present it sufficiently influences the net result so that the latter is represented by an adsorption equation.

True adsorption is nearly instantaneous. Any lag is at present accounted for by the time required for the dissipation of the heat evolved, or by the comparative inaccessibility of a portion of the surface of a porous adsorbing agent. On the other hand, absorption, or solid solution, may be expected to follow Fick's diffusion law which requires that it should commence with a very high velocity for the first few moments but rapidly fall off with time, and, theoretically, require infinite time for perfect equilibrium to be attained.

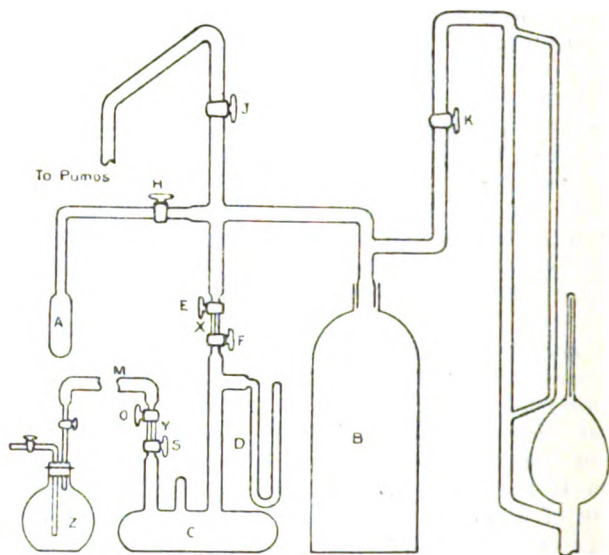
While performing experiments to determine the amount of carbon dioxide adsorbed by activated coconut charcoal \*, it was noted that at very low pressures this gas required a considerable time to attain equilibrium; rapid adsorption took place during the first few minutes but was followed by slow absorption during the succeeding 24 hours. Most of the gas was adsorbed during the first stage, and the slow absorption that followed did not materially affect the volume taken up, but the final pressure attained depended primarily on the time during which the gas was in contact with the charcoal. This effect has been studied and the results obtained are given below.

\* See H. Rowe, *Phil. Mag.* i. p. 109 (1926).

## 2. Experimental Arrangement.

The apparatus used in carrying out the experiments (fig. 1) was similar to that used for measuring the amounts of various gases adsorbed by activated charcoal at very low pressures\*.

Fig. 1.



The coconut charcoal had been activated by the steam process, but before use it was reactivated by the "air-oxidation" treatment. This was effected by placing a shallow layer of the charcoal in a silica tube, open at both ends, and having an electric heating coil wound round it. The charcoal was heated to  $450^{\circ}\text{C}$ . for half-an-hour and air blown over its surface from time to time. A sample that had been used previously to measure the adsorption of carbon monoxide was employed to determine the rate of adsorption of carbon dioxide. This sample was completely outgassed by heating to  $450^{\circ}\text{C}$ . for 8 hours, the mercury-vapour pump backed by an oil pump working continuously to remove any gases liberated during this outgassing. The charcoal was tested for complete outgassing by allowing it to cool, the tap H being closed and the system being at a pressure less than  $10^{-5}$  mm.† The charcoal was then

\* *Loc. cit.*

† Pressures are expressed in mm. of mercury.

reheated to  $450^{\circ}\text{C}$ . for half-an-hour with the tap H open, the pumps being disconnected, and if no increase in pressure resulted it could be safely assumed that outgassing was complete.

Carbon dioxide was prepared by the action of pure hydrochloric acid on freshly boiled air-free marble in a Wolff bottle, and after passing over calcium chloride and phosphorus pentoxide to remove the excess of water-vapour it entered a small bulb Z having taps on the inlet and outlet tubes. A rapid stream of carbon dioxide was passed through the bulb for two hours, before closing the taps, to ensure the complete removal of atmospheric gases. The bulb Z containing the gas to be used was sealed to M and the whole of the apparatus exhausted to a pressure below  $10^{-5}$  mm. Tap F was then closed and gas from Z admitted to the reservoir C by alternately opening and closing the taps O and S. In this way the gas pressure in C was raised to a convenient value.

The actual rate of adsorption of carbon dioxide was measured in the following manner. After the charcoal had been completely outgassed and the high vacuum side exhausted to  $10^{-5}$  mm., tap H was closed and the pumps shut off. The gas was then admitted to the high vacuum side from the reservoir C by opening and closing taps E and F, so that the small volumes of gas trapped between these taps could be allowed to enter the high vacuum side. Sufficient gas was admitted to bring the pressure to any desired value, and after a period of 30 minutes during which equilibrium was attained, the pressure was noted on a McLeod gauge. Tap H was then opened and the pressure measured at stated intervals of time, the time of opening the tap H being taken as zero. After carrying out one series of readings the charcoal was completely outgassed by heating to  $450^{\circ}\text{C}$ . for 12 hours, and a new series of readings taken commencing at a different initial pressure. Great care was taken that the time and temperature were the same in all the experiments, so that the initial condition of the charcoal was as nearly as possible the same in all the experiments. The air temperature was read at one hour intervals and the average value noted. Throughout all the experiments its mean value was  $20^{\circ}\text{C}$ .

### *3. Experimental Results,*

In all, six experiments were made at various initial pressures ranging from  $2 \times 10^{-2}$  mm. to  $1.5 \times 10^{-1}$  mm.

The results obtained are given in Table I., where  $t$  is

TABLE I.—Rate of Adsorption of Carbon Dioxide at 20° C.

EXPERIMENT 1.			EXPERIMENT 2.		
<i>t.</i>	<i>p.</i>	<i>q.</i>	<i>t.</i>	<i>p.</i>	<i>q.</i>
0 min.	$36.97 \times 10^{-3}$ mm.	c.c. 0	0 min.	$92.61 \times 10^{-3}$ mm.	c.c. 0
2	24.93	6.506	2	59.78	17.76
15	3.494	18.11	15	15.33	41.05
30	1.742	19.06	30	11.46	43.91
60	1.349	19.27	60	9.607	44.91
120	1.161	19.37	120	7.652	45.98
360	1.158	19.38	360	5.118	47.38
1440	1.134	19.39	1440	4.178	47.86

EXPERIMENT 3.			EXPERIMENT 4.		
<i>t.</i>	<i>p.</i>	<i>q.</i>	<i>t.</i>	<i>p.</i>	<i>q.</i>
0 min.	$141.8 \times 10^{-3}$ mm.	c.c. 0	0 min.	$113.8 \times 10^{-3}$ mm.	c.c. 0
2	87.36	29.48	2	74.97	21.12
15	26.56	62.38	15	23.85	48.59
30	22.20	64.74	30	18.26	51.70
60	19.54	66.19	60	15.41	53.25
90	18.09	66.97	90	13.93	54.04
120	17.19	67.45	180	11.69	55.26
240	14.86	68.73	300	9.630	56.37
1140	9.82	71.45	1080	6.149	58.25
1440	9.50	71.63	1440	5.758	58.46

EXPERIMENT 5.			EXPERIMENT 6.		
<i>t.</i>	<i>p.</i>	<i>q.</i>	<i>t.</i>	<i>p.</i>	<i>q.</i>
0 min.	$63.38 \times 10^{-3}$ mm.	c.c. 0	0 min.	$24.67 \times 10^{-3}$ mm.	c.c. 0
2	40.26	12.51	2	16.81	4.253
15	8.814	29.53	15	2.065	12.23
30	6.306	30.89	30	0.873	12.88
60	5.1	31.53	60	0.702	12.97
120	4.108	32.07	90	0.695	12.97
280	3.346	32.49	930	0.695	12.97
510	2.701	32.84	1440	0.695	12.97
1440	1.966	33.24			

the time in minutes,  $p$  is the pressure in mm., and  $q$  the quantity of gas adsorbed per gram of charcoal, expressed in c.c. at 1 mm. pressure and  $20^{\circ}\text{C}$ ., is given by

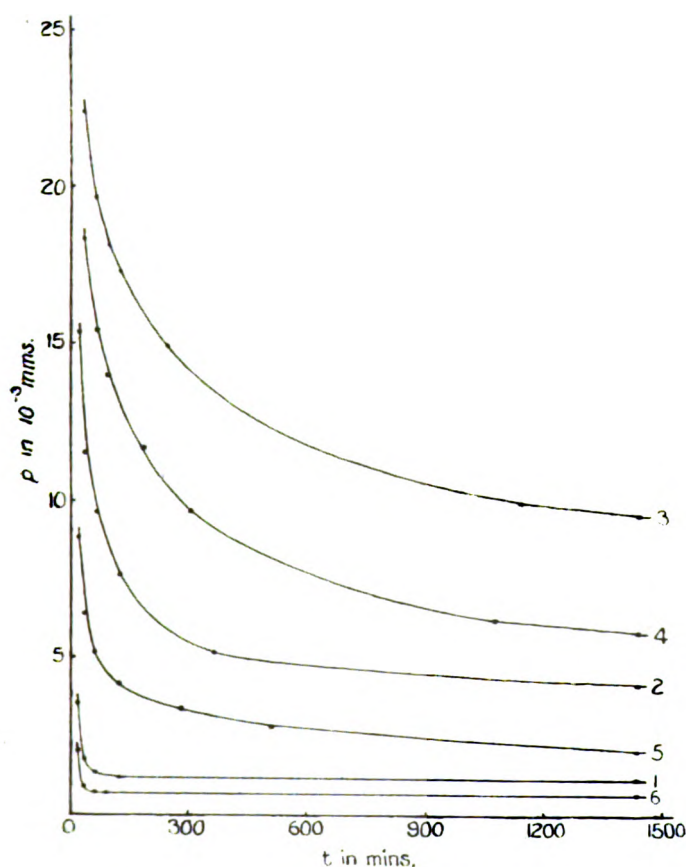
$$q = \frac{V}{m} (p_0 - p),$$

where  $V$  = volume of high vacuum side = 3160 c.c.

$m$  = mass of charcoal = 5.84 grms.

$p_0$  = initial pressure in mm.

Fig. 2.



Rate of Adsorption of  $\text{CO}_2$  at Various Pressures.  
Charcoal completely outgassed.

The graphical relation between pressure and time is shown in fig. 2.



An examination of the curves shows that as the initial and equilibrium pressures increase the time required for equilibrium to be attained becomes greater. The curves consist of two distinct portions, one part being almost vertical and the other tending to a horizontal direction. There is no sudden discontinuity in these parts, but they are joined by a smooth curve. Undoubtedly the rapid lowering of pressure with time that occurs in the first 30 minutes, and is represented by the almost vertical portion of the curves, is due primarily to *adsorption* forces, while the horizontal portion of the curves must be attributed, if McBain's theory is correct, to an *absorption* process taking place. *Absorption* follows a similar law to Fick's diffusion law. *i. e.* it is of exponential form, rapidly decreasing with time, but *adsorption* occurs so rapidly that it completely masks any *absorption* that may be present, and until *adsorption* has ceased the function of *absorption* cannot be detected. If  $\log p/p_0$  is plotted against  $t$  for the various results it is found that for the portion between  $t=60$  and 1440 minutes a straight line is obtained, thus showing that the lowering of pressure over this time interval is due solely to *adsorption* forces.

The process of *absorption* must depend not only on the pressure of the gas outside the charcoal but also on the concentration within the charcoal, for *absorption* consists of the passing of gas into the finer capillaries of the charcoal after the coarser ones have been filled by *adsorption* processes. The gas concentration in the coarser capillaries is then renewed by the *adsorption* of gas from the outside, and this continues until equilibrium is attained. In this respect *absorption* does not follow exactly the diffusion law, for experiment indicates that it reaches a limit in a measurable time, whereas the diffusion law states that infinite time is required for equilibrium to be attained.

From Table I., Experiment 6, it will be noted that the equilibrium pressure is attained after an interval of one hour, and that part of the curve shown in fig. 2 No. 6 which refers to *absorption* is represented by a horizontal straight line. It is inferred from this that below  $0.70 \times 10^{-3}$  mm. there is no *absorption*; all gas within the sorbate being held by *adsorption* forces. The time required for this *adsorption* effect to be complete depends upon various factors. The actual rate of *adsorption* depends upon the dimensions of the apparatus, since at the very low pressures employed the mean free path of the gas molecules

is comparable with the dimensions of the apparatus, and a definite time will be required for the gas molecules to diffuse from the main volume to the charcoal bulb, where they replace those molecules of gas that have been absorbed. With the apparatus used *adsorption* was complete after 60 minutes approximately.

Investigations on the adsorptive capacity of charcoal for carbon dioxide, the charcoal containing some adsorbed gas, were made and the results are given in Table II.

TABLE II.

## Rate of Adsorption of Carbon Dioxide at 15° C.

*Experiment 1.*

Initial conditions: Charcoal contained 36.32 c.c.—at 1 mm. pressure and 15° C.—per gram at an equilibrium pressure of  $1.745 \times 10^{-3}$  mm.

<i>t.</i>	<i>p.</i>	<i>q.</i>
0 min.	$18.65 \times 10^{-3}$ mm.	0 c.c.
5	9.537	4.865
30	6.387	6.549
90	5.532	7.004
210	4.842	7.372
330	4.217	7.715
450	3.835	7.912
1440	2.515	8.614

*Experiment 2.*

Initial conditions: Charcoal contained 44.93 c.c.—at 1 mm. pressure and 15° C.—per gram at an equilibrium pressure of  $2.515 \times 10^{-3}$  mm.

<i>t.</i>	<i>p.</i>	<i>q.</i>
0 min.	$24.97 \times 10^{-3}$ mm.	0 c.c.
5	13.29	6.210
30	9.764	8.108
60	9.312	8.351
150	8.416	8.831
270	7.561	9.283
390	7.100	9.532
510	6.444	9.881
1440	4.494	10.92

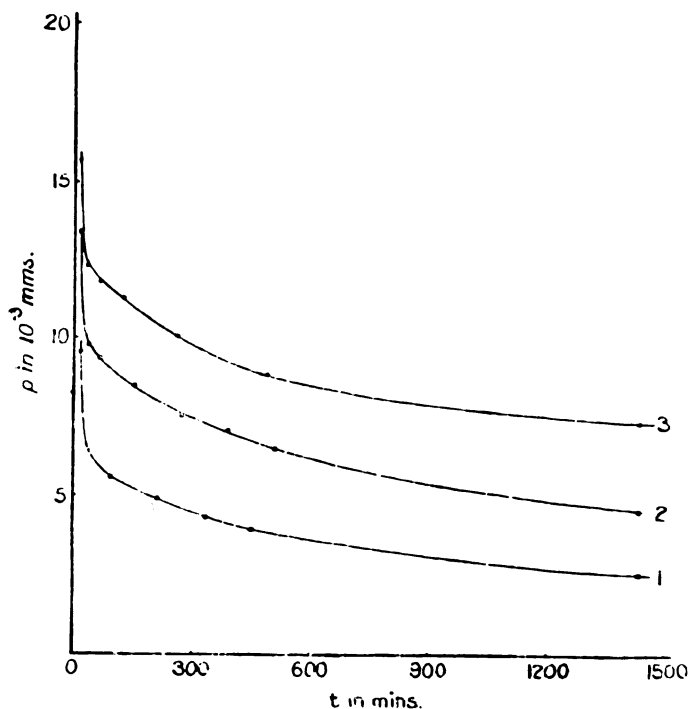
TABLE II. (continued).

*Experiment 3.*

Initial Conditions: Charcoal contained 56.10 c.c.—at 1 mm. pressure and 15° C.—at an equilibrium pressure of  $4.250 \times 10^{-3}$  mm.

<i>t.</i>	<i>p.</i>	<i>q.</i>
0 min.	$26.69 \times 10^{-3}$ mm.	0 c.c.
5	15.52	5.964
30	12.27	7.703
60	11.77	7.968
120	11.22	8.258
260	10.01	8.902
360	9.165	9.354
490	8.840	9.528
1440	7.310	10.35

Fig. 3.



Rate of Adsorption of  $\text{CO}_2$  at Various Pressures.  
Charcoal not completely outgassed.

The results given in Table II. have been plotted and are shown in fig. 3. Considering these curves it will be noted

that they are similar to those given in fig. 2, but the *absorption* portion is more pronounced. Owing to the fact that the charcoal already contains some gas the quantity adsorbed from the surrounding gas will be considerably less and adsorption takes place very rapidly, so that after an interval of 15 minutes the *adsorption* process fails to mask the *absorption* phenomenon.

#### 4. Discussion.

If *absorption* depends on the concentration of the gas in the charcoal, then it is quite possible that there will be a limiting value of this concentration below which *absorption* cannot take place. According to Langmuir\* the first process in sorption is the formation of a monomolecular film on the surface of the sorbate. It is highly improbable that this is removed by *absorption* forces, and the presence of this film would account for no *absorption* taking place in Experiment 6 and very little in Experiment 1. Accordingly a value in the region of 13-16 c.c.—measured at 1 mm. pressure and 20° C.—may be taken as the limiting value of the gas concentration in the charcoal below which *absorption* cannot occur.

In general it is recognized that both *adsorption* and *absorption* commence simultaneously when outgassed charcoal is placed in contact with a gas, but if the above view is accepted then it must be inferred that though *adsorption* begins immediately, *absorption* will only commence after this definite concentration has been reached. At very high initial pressures this concentration would be attained almost immediately, so that for all practical purposes the two processes do commence at one and the same time at high pressures.

In Experiments 1 and 6, one-third of the total quantity sorbed is taken up in the first two minutes, and in each case this quantity is less than the minimum quantity adsorbed, but in the other experiments more than one-third is taken up in the same time and is, in each case, always greater than the minimum value. This fact seems to indicate that both processes occur at higher pressures, but *adsorption* only is the determining factor at very low pressures.

No rational expression for the variation in the rate of sorption described above has yet appeared. In fact, even an empirical analytical expression has not been formulated. The phenomena here described are of such complexity that it seems desirable to simplify experimental conditions and to secure more data before attempting to express a theory.

\* Phys. Rev. viii. p. 149 (1916).

5. *Summary.*

1. While investigating the adsorptive capacity of activated coconut charcoal for carbon dioxide at very low pressures it was found that time effects came into operation, and a definite time was required for equilibrium pressure to be attained.

2. The rate of *adsorption* of carbon dioxide by outgassed charcoal at various initial pressures was measured.

3. It was found that in general *adsorption* and *absorption* processes were both present, but that below a definite equilibrium pressure, and definite concentration of the gas in the charcoal, *adsorption* alone was operative.

4. *Absorption* does not begin at the same time as *adsorption* but only when the concentration of the gas in the charcoal has reached this limiting value.

In conclusion the author wishes to express his sincere thanks to Prof. F. H. Newman for suggesting this branch of research and for the keen interest he has taken and the helpful suggestions made throughout.

LVI. *On the "Hypothetical Infinite Population" of Theoretical Statistics.* By W. BURNSIDE, F.R.S.\*

**I**N a memoir on the Mathematical Foundation of Theoretical Statistics (Phil. Trans. vol. ccxxii.), Mr. R. A. Fisher, having stated that the object of statistical methods is the reduction of data, goes on (p. 311) :

"This object is accomplished by constructing a hypothetical infinite population, of which the actual data are regarded as constituting a random sample. The law of distribution of this hypothetical population is specified by relatively few parameters, which are sufficient to describe it exhaustively in respect of all qualities under discussion."

It is essential that the conception conveyed by the phrase "hypothetical infinite population," which is here introduced as one of the bases of theoretical statistics, should be the same for all who make use of it. Beyond the passage quoted above, nothing further occurs in Mr. Fisher's memoir to give precision to this conception. Readers of the memoir are thus thrown back upon the quoted passage to form their own conception of a "hypothetical infinite population."

\* Communicated by the Author.

Now a statistical table, abstractly considered, consists of a finite number of distinct individuals, classified in respect of a finite number of classes. The simplest possible form of such a table will consist in the statement that in a collection of a finite number  $N$  of distinct individuals,  $N_A$  belong to class A, and the remaining  $N - N_A$  do not belong to class A. Of what "hypothetical infinite populations" can this collection be regarded as a random sample? In the first place the "population" must consist of individuals, each two of which can be distinguished from each other, since this is a property of a random sample; and for the same reason, it must be known with respect to each individual of the "population" whether it does or does not belong to class A.

The first sentence in the passage quoted then leads to the conclusion that in this simplest case the "hypothetical infinite population" is a collection of distinct individuals which is classified in respect of class A.

It is less easy to be sure as to what is implied in regard to the "population" by the second sentence of the passage quoted. In this simplest case the quality under discussion is belonging or not belonging to class A. In the sample  $N_A/N$  of the individuals composing it belong to class A. This fraction is the frequency (or frequency-ratio) of individuals belonging to class A in the sample. It would seem that the most probable meaning of the second sentence in the passage quoted is that there is a proper fraction  $f$  which gives the same information with respect to the "hypothetical infinite population" that the fraction  $N_A/N$  gives with respect to the sample. The assumption that such a fraction as  $f$  exists is of the nature of an hypothesis, since a frequency-ratio is originally defined in connexion with a finite collection of individuals. This may account for the use of the word hypothetical in describing the population.

During the last thirty years there has been a large amount of valuable work in connexion with the properties of, and the relations between, collections of distinct individuals. Among the results which command the assent of all mathematicians are the following:—

With regard to a collection of distinct individuals, there are the following mutually exclusive possibilities. Either

- (i.) it can be counted and the counting terminates; or
- (ii.) it can be counted and the counting does not terminate; or
- (iii.) it cannot be counted.

Further, between the individuals of any two collections which come under head (ii.) a one-to-one correspondence can be set up.

If a "hypothetical infinite population" comes under head (i.), it can only be said that the word "infinite" in its description has been unfortunately chosen. It, like the sample drawn from it, consists of a finite number of distinct individuals.

If a "hypothetical infinite population" comes under head (ii.), a one-to-one correspondence can be set up between the individuals constituting it and the collection of all positive integers. In this case the question whether the frequency-ratio of a class in "hypothetical infinite population" has any definite meaning may be replaced by the question whether the frequency-ratio of a specified class of integers in the collection of all integers has a definite meaning.

Now a specified class of integers can certainly be counted and there are the two alternatives that the counting (i.) terminates, (ii.) does not terminate. In the first case the specified class consists of a finite number  $N$  of integers. If a finite collection of integers is formed by combining with the  $N$  integers of the specified class  $M$  integers which do not belong to the class, the frequency-ratio of the specified class in this finite collection is  $N/(N+M)$ . No matter how the  $M$  integers are chosen, this fraction approaches the limit zero as the number  $M$  is taken larger and larger. It may be said then, in a quite definite sense, that when the specified class consists of a finite number of integers the frequency-ratio of the class in the totality of integers is zero. The statement that the frequency-ratio of a specified class of integers is zero does not, however, imply, as it would in dealing with a finite collection, that there are no individuals in the class. All that can be inferred is that if there are individuals in the class their number is finite.

Suppose now in the second case that the counting of the specified class does not terminate. A particular illustration of a class of this kind is the class of integers which are divisible by 7. If we suppose all integers arranged in order of magnitude and take the first  $N$  as a finite collection, the frequency-ratio of the specified class in the finite collection of  $N$  will, when  $N$  is large compared to 7, be very nearly  $\frac{1}{7}$ . If  $N$  is taken large enough it can be insured that the frequency-ratio of the specified class in the collection of  $N$  differs from  $\frac{1}{7}$  by as small an amount as desired.

The order of magnitude is only one very particular way

of arranging all integers. Another arrangement is that indicated by

1, 7, 2, 14, 3, 21, 4, 28, 5, 35, 6, 42, 8, 49, 9, 56, 10, 63,  
11, 70, 12, 77, 13, 84, 15, 91, ..... .

In this arrangement every integer occurs in one definite place, and no integer occurs twice.

If here the first  $N$  are taken as a finite collection, and  $N$  is large enough, the frequency-ratio of the specified class in the collection of  $N$  differs from  $\frac{1}{2}$  by as small an amount as desired.

A precisely similar process may be used with any specified class which is not finite. The totality of integers may be arranged in a definite sequence in which each integer occurs once and no integer occurs twice, so that the first  $a$  do not belong to the specified class, the next  $b$  do, the next  $a$  do not, the next  $b$  do, and so on. If here the first  $N$  are taken as a finite collection, and  $N$  is large enough, the frequency-ratio of the specified class in the collection of  $N$  differs from  $b/(a+b)$  by as small a quantity as desired.

What precedes justifies the following statement :—

When the "hypothetical infinite population" comes under head (ii.) it is not possible to obtain a unique value, other than zero, for the frequency-ratio of a specified class by calculating the frequency-ratio  $f_N$  of the class in a collection of  $N$  from the population, and determining the limit of  $f_N$  as  $N$  increases. This statement is not inconsistent with the further statement that "the frequency-ratio of a specified class in a hypothetical infinite population" is a phrase without meaning. The second sentence in the passage quoted from Mr. Fisher's memoir, if I have interpreted it correctly, implies that the author regards "the frequency-ratio of a specified class in a hypothetical infinite family" as a phrase with a perfectly definite meaning, and in any particular case a perfectly definite value. From this point of view the following question immediately suggests itself. What is the value of the frequency-ratio of the class of integers divisible by 7 in the collection of all integers, and what information does a knowledge of the value of this frequency-ratio give? So long as this question remains unanswered, it is a mere assumption to suppose that "the frequency-ratio of a specified class in a hypothetical infinite population" is a phrase with a definite meaning.

*Phil. Mag.* S. 7. Vol. 1. No. 3. March 1926. 2 X



There remains the possibility that a "hypothetical infinite population" comes under head (iii.). If this is the case, the difficulties that arise in attaching a definite meaning and a definite value to the frequency-ratio of a specified class are certainly not less than in the case already considered, for it is not possible to approach such a collection directly from a collection which can be counted.

LVII. *The Vibrations of Rods and Shafts with Tension or End-Thrust.* By R. C. J. HOWLAND, M.A., M.Sc., *University College, London* \*.

### 1. *Introductory.*

THE determination of the whirling speeds of shafts subjected to an axial thrust or tension is of importance in the theory of some types of modern machinery, while a knowledge of the natural periods of vibration of rods in a state of longitudinal stress is needed when the stability of a framed structure is considered. The two problems are mathematically identical. In the general case, when the rod or shaft is not uniform or when it carries an unevenly distributed mass, the differential equation from which the critical states are to be determined cannot be integrated in a finite form.

For a rod or shaft without end-thrust or tension, a method for reducing the integration to a series of quadratures was given by Messrs. Cowley and Levy †. Their method solves the equation in a series in powers of a parameter which is a multiple of the square of the whirling speed or of the frequency. The method is essentially a particular application of the method of successive approximation which, in various forms, has been used at least since the time of Laplace. A general theory is given by Picard ‡ and repeated by Bateman §. Expansions in powers of a parameter occur in the theory of integral equations ||. A solution of certain

\* Communicated by the Author.

† "On a Method of Analysis suitable for the Differential Equations of Mathematical Physics," *Phil. Mag.* xli. April 1921.

‡ E. Picard, '*Traité d'Analyse*,' t. ii. 2nd ed. p. 340 (1905).

§ H. Bateman, '*Differential Equations*,' p. 245 (1918).

|| See, for example, Whittaker & Watson, '*Modern Analysis*,' 3rd ed. p. 213 (1920).

differential equations in a series in powers of parameters was given by Baker\*, who traces his method back to Caqué† and Fuchs‡. Caqué's solution of the general linear equation in terms of iterated functions obtained by a sequence of integrations has affinities to the method of the present paper §.

A special application of the method of Cowley and Levy to determine the whirling speeds of a shaft carrying concentrated masses was made by the present writer in a recent paper ||. A theoretical deduction of Dunkerley's Rule was given and the magnitude of the error involved in the use of this rule was investigated.

In the present paper the same method is applied to the more general problem of a rod or shaft under axial force. By the assumption of a double series in powers of two parameters a solution is found which, involving only quadratures, is suitable for graphical or numerical calculation. The method is illustrated by applying it to a uniform shaft, and the results are compared with those given by an exact integration. An application to rods and shafts carrying concentrated masses is then made and the error in Dunkerley's Rule is calculated for a number of different end-thrusts and tensions. The method is both rigorous and general.

Only special cases of the general problem appear to have received attention previously. The vibrations of a uniform bar under tension were considered by Clebsch¶, and the same analysis has been applied to the problem of whirling\*\* and to that of the stability of a rotating shaft under end-thrust††. The vibrations of struts with several supports and uniform in each bay have been considered by Cowley and

\* H. F. Baker, "On Certain Linear Differential Equations of Astronomical Interest," *Phil. Trans. A*, ccxvi. pp. 129-186 (1916).

† M. J. Caqué, "Méthode nouvelle pour l'intégration des équations différentielles linéaires," *Liouville's Journal*, 2nd ser. t. ix. pp. 185-222 (1864).

‡ Fuchs, *Ann. d. Mat.* 2nd ser. t. iv. p. 36.

§ Cf. also a series of papers by E. & F. Cosserat, *Comptes Rendus*, cxvi. (1898) and cxxiii. (1901).

|| "The Whirling Speeds of Shafts Carrying Concentrated Masses," *Phil. Mag.* xlix. p. 1131 (1925).

¶ Clebsch, "Theorie der Elasticität fester Körper," Chap. iv. § 61, or in the French translation of de St. Venant, p. 480 gg. See also Rayleigh, 'Theory of Sound,' 2nd ed. p. 296.

\*\* See, for example, Morley, 'Strength of Materials,' 5th ed. p. 464.

†† H. Mawson, "Struts and Tie-Rods in Motion," *Proc. Inst. Mech. Eng.* 1915, p. 433.

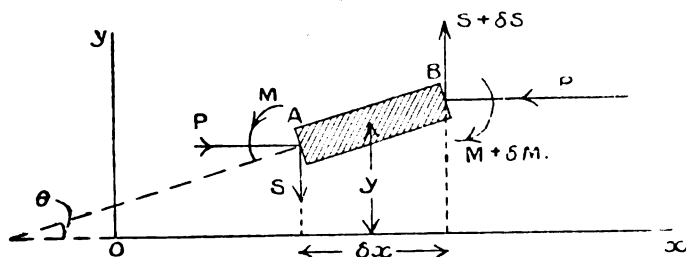
Levy\*, using the general equations, and by Shôgenji†, using Rayleigh's approximate method. The whirling speed of a shaft axially loaded and carrying a central mass was considered by Melan‡ by Ritz's minimum energy method. More recently Schwerin§ has obtained interesting results in the same problem by using the full expression for the curvature of the shaft, thus extending the work of v. Mises|| on the shaft without end-thrust. But no general method for calculating the whirling speeds of non-uniform shafts or the vibration periods of non-uniform rods under axial forces appears to have been published.

## 2. The Differential Equation.

Consider a shaft specified as follows:—

Young's Modulus .....	$E$
Density of Material .....	$\rho$
Area of Cross-section .....	$A$
Second Moment of Cross-section ...	$I = Ak^2$
End-thrust .....	$P$
Angular Velocity .....	$\omega$
Distance from a chosen end .....	$x$
Deflexion .....	$y$

Fig. 1.



Let  $M$  be the bending moment,  $S$  the stress resultant parallel to the axis of  $y$ ;  $P$ , the stress resultant parallel to the axis of  $x$ , is constant.

\* Cowley & Levy, "Vibration and Strength of Struts and Continuous Beams under End-Thrusts," Proc. Roy. Soc. A, vol. xcv. (1918).

† Shôgenji, "Approximate Calculation of the Natural Period of Rods," Mem. Coll. Eng. Kyushu, vol. iii. No. 3 (1924).

‡ H. Melan, "Kritische Drehzahlen von Wellen mit Längsbelastung," Zeit. Oest. Ing. u. Arch. Ver. xlv. p. 45 (1917).

§ E. Schwerin, "Die Stabilität rotierender achsial belasteter Wellen," Zeit. f. ang. Math. u. Mech. v. p. 101 (1925).

|| R. v. Mises, Monatshefte f. Math. u. Phys. 1911, p. 44.

Then the equations of motion of the element AB (fig. 1) are :—

- (1) From acceleration parallel to  $y$ -axis,

$$\rho A \delta x (\ddot{y} - y\omega^2) = \delta S.$$

- (2) From rate of change of angular momentum,

$$\rho A \delta x [k^2 + (\frac{1}{2} \delta x)^2] \dot{\theta} = \delta M + P \frac{dy}{dx} \delta x + S \delta x,$$

or, when  $\delta x \rightarrow 0$ ,

$$\rho A (\ddot{y} - y\omega^2) = \frac{dS}{dx}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\rho I \frac{d^3 y}{dt^2 dx} = \frac{dM}{dx} + P \frac{dy}{dx} + S. \quad . \quad . \quad . \quad (2)$$

To these may be added the usual relation between curvature and bending moment,

$$M = EI \frac{d^2 y}{dx^2}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Differentiating (2) with regard to  $x$  and substituting from (1) and (3) for  $\frac{dS}{dx}$  and  $M$ , we have

$$\frac{d}{dx} \left( \rho I \frac{d^3 y}{dx dt^2} \right) = \frac{d^3}{dx^2} \left( EI \frac{d^2 y}{dx^2} \right) + P \frac{d^2 y}{dx^2} + \rho A \left( \frac{d^3 y}{dt^2} - y\omega^2 \right), \quad (4)$$

where  $\rho I$ ,  $EI$ ,  $\rho A$  are, in general, functions of  $x$ .

If the rotating shaft executes vibrations of frequency  $\sigma$ , the equation becomes

$$\begin{aligned} \frac{d^2}{dx^2} \left( EI \frac{d^2 y}{dx^2} \right) + 4\pi^2 \sigma^2 \frac{d}{dx} \left( \rho I \frac{dy}{dx} \right) \\ + P \frac{d^2 y}{dx^2} - \rho A (4\pi^2 \sigma^2 + \omega^2) y = 0. \quad . \quad (5) \end{aligned}$$

For the case of a rod without rotation, we have  $\omega^2 = 0$ ; while, for a shaft at one of its whirling speeds, one vibration frequency becomes zero and the equation is

$$\frac{d}{dx^2} \left( EI \frac{d^2 y}{dx^2} \right) + 4\pi^2 \sigma^2 \frac{d}{dx} \left( \rho I \frac{dy}{dx} \right) + P \frac{d^2 y}{dx^2} - \rho A \omega^2 y = 0. \quad (6)$$

The nature of the parameters involved is made clearer if

the coordinates are made non-dimensional. This is accomplished by using the transformation,

$$\left. \begin{aligned} x &= lx' \\ y &= ly' \\ \rho A &= \rho_0 A_0 f(x') \\ EI &= E_0 I_0 \phi(x') \\ \rho I &= \rho_0 I_0 \psi(x'), \end{aligned} \right\} \dots \dots \dots (7)$$

where  $l$  is any fixed length and will be taken to be the whole length of the shaft, and  $\rho_0, A_0, E_0, I_0$  are the values of  $\rho, A, E, I$  at some selected point, say the origin. Making this substitution and then dropping the dashes, we find

$$\frac{d^2}{dx^2} \left\{ \phi(x) \frac{d^2 y}{dx^2} \right\} + q^2 \frac{d}{dx} \left\{ \psi(x) \frac{dy}{dx} \right\} + p^2 \frac{d^2 y}{dx^2} - \theta^4 f(x)y = 0, \quad \dots \dots (8)$$

in which

$$\left. \begin{aligned} q^2 &= \frac{\rho_0 l^2}{E_0} \cdot 4\pi^2 \sigma^2, \\ p^2 &= \frac{Pl^2}{E_0 I_0}, \\ \theta^4 &= \frac{\rho_0 A_0 l^4}{E_0 I_0} (4\pi\sigma^2 + \omega^2); \end{aligned} \right\} \dots \dots \dots (9)$$

$q, p$  and  $\theta$  are pure numbers, non-dimensional in mass, length and time, and (8) is expressed wholly in terms of non-dimensional quantities. When the shaft is in tension,  $p^2$  is negative.

It is interesting to note that, in the case where  $\rho I$  is constant, the only effect of the rotatory inertia term is to increase the effective end-thrust  $P$ . When  $\sigma=0$ , *i. e.* for a steady deflexion at a whirling speed, this term disappears from the equation. In other cases, it is usually small and in what follows it will be neglected. The equation then takes the form

$$\frac{d^2}{dx^2} \left\{ \phi(x) \frac{d^2 y}{dx^2} \right\} + p^2 \frac{d^2 y}{dx^2} - \theta^4 f(x)y = 0, \quad \dots (10)$$

together with the end conditions

$$\begin{aligned} y &= 0 \quad \text{when } x = 0 \text{ or } 1, \\ \frac{d^2y}{dx^2} &= 0 \quad \text{when } x = 0 \text{ or } 1, \text{ (short bearing),} \\ \text{or } \frac{dy}{dx} &= 0 \quad \text{when } x = 0 \text{ or } 1, \text{ (long bearing).} \end{aligned}$$

In all the problems considered, it is required to find for what values of the parameters the equation has a non-zero solution. Usually  $p^2$  is regarded as known and  $\theta^4$  is sought. The inverse problem is also of interest. Given  $\theta^4$  we may attempt to find  $p^2$  and hence the critical values of the thrust under which the shaft will tend to buckle if, while rotating with a given angular velocity, it is subject to a forced vibration of known frequency. For such purposes a solution of (10) in a series in powers of the parameters  $p^2$  and  $\theta^4$  is convenient.

### 3. *Solution by Quadratures.*

The required development may be found in a form involving only quadratures by the following method.

Let

$$y = Ay_1 + By_2 + Cy_3 + Dy_4 \dots \dots \dots (11)$$

be the complete primitive of the differential equation

$$\frac{d^2}{dx^2} \left\{ \phi(x) \frac{d^2y}{dx^2} \right\} = 0,$$

and denote the integral operators

$$\begin{aligned} &\int_0^x dx \int_0^x \frac{dx}{\phi(x)} \\ \text{and } &\int_0^x dx \int_0^x \frac{dx}{\phi(x)} \int_0^x dx \int_0^x dx f(x) \end{aligned}$$

by  $\alpha$  and  $\beta$  respectively.

Then if (11) is taken as a first approximation to a solution of (10) and is substituted in the second and third terms of (10), a second approximation is obtained by integration in the form

$$A\{y_1 + (\theta^4\beta - p^2\alpha)y_1\} + B\{y_2 + (\theta^4\beta - p^2\alpha)y_2\} + \text{etc.}$$

Repeating this process we obtain a third approximation,

$$A\{y_1 + (\theta^4\beta - p^2\alpha)y_1 + (\theta^4\beta - p^2\alpha)^2y_1\} + B\{\dots\} + \text{etc.}$$

and so on.

It must be noted that, in developing a power  $(\theta^4\beta - p^2\alpha)^n$  we have  $n^2$  terms, since  $\alpha\beta$  and  $\beta\alpha$  are distinct.

The above process leads to four infinite series of the type

$$y = y_n + (\theta^4\beta - p^2\alpha)y_n + (\theta^4\beta - p^2\alpha)^2y_n + \text{etc.} \quad (12)$$

$n = 1, 2, 3, 4.$

It will now be verified that each series gives a solution of the differential equation. For, apply to  $y$  the operator

$$\frac{d^2}{dx^2}\phi(x)\frac{d^2}{dx^2},$$

assuming, for the moment, that it is legitimate to apply it term by term. Then, since

$$\frac{d^2}{dx^2}\phi(x)\frac{d^2}{dx^2}y_n = 0$$

$$\text{and} \quad \frac{d^2}{dx^2}\phi(x)\frac{d^2}{dx^2}(\theta^4\beta - p^2\alpha) \equiv \theta^4 - p^2\frac{d^2}{dx^2},$$

we have at once

$$\begin{aligned} \left(\frac{d^2}{dx^2}\phi(x)\frac{d^2}{dx^2}\right)y &= \left(\theta^4 - p^2\frac{d^2}{dx^2}\right)[y_n + (\theta^4\beta - p^2\alpha)y_n + \dots] \\ &= \left(\theta^4 - p^2\frac{d^2}{dx^2}\right)y, \end{aligned}$$

and the equation is formally satisfied.

This procedure will be justified if it can be proved that the result of term by term differentiation is uniformly convergent, *i. e.* that

$$\left(\theta^4 - p^2\frac{d^2}{dx^2}\right)y$$

is a uniformly convergent series.

Now  $\phi(x)$  is a positive, bounded function in the interval  $0 < x < 1$ . If its lower bound is  $\lambda$  we may write

$$\left. \begin{aligned} y_1 &= 1, \\ 0 &< y_2 = x < 1, \\ 0 &< y_3 = \int_0^x dx \int_0^x \frac{dx}{\phi(x)} < \frac{1}{\lambda} \cdot \frac{x^2}{2} < \frac{1}{\lambda}, \\ 0 &< y_4 = \int_0^x dx \int_0^x \frac{x dx}{\phi(x)} < \frac{1}{\lambda} \cdot \frac{x^3}{3} < \frac{1}{\lambda}, \end{aligned} \right\} \quad \dots \quad (13)$$

so that all the functions  $y_1, y_2, y_3, y_4$  are positive and bounded.

Again,  $f(x)$  is a positive, bounded function in the interval considered. If  $\mu$  be its upper bound and if  $\psi(x)$  be any positive function having an upper bound  $K$  in the interval, it is evident that

$$\begin{aligned} 0 < \beta \psi(x) &\leq \frac{\mu K}{\lambda} \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x dx \\ &= \frac{\mu K}{\lambda} \cdot \frac{x^4}{4} \end{aligned}$$

and

$$\begin{aligned} 0 < \alpha \cdot \psi(x) &\leq \frac{K}{\lambda} \int_0^x dx \int_0^x dx \\ &= \frac{K}{\lambda} \cdot \frac{x^2}{2}. \end{aligned}$$

Thus

$$\begin{aligned} |(\theta^4 \beta - p^2 \alpha) \psi(x)| &\leq \frac{K}{\lambda} \cdot \frac{x^2}{2} \left( p^2 + \frac{\mu \theta^4 x^2}{12} \right) \\ &\leq K \left| \frac{x^2}{2} \right| \nu, \end{aligned}$$

where  $\nu = \left( p^2 + \frac{\mu \theta^4}{12} \right) \cdot \frac{1}{\lambda}$ , since  $x^2 \leq 1$ .

Again, we have, for  $m \geq 2$ ,

$$\begin{aligned} 0 < \beta \cdot \frac{x^m}{m} &\leq \frac{\mu}{\lambda} \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x \frac{x^m}{m} dx \\ &= \frac{\mu}{\lambda} \frac{x^{m+4}}{m+4}, \end{aligned}$$

$$\begin{aligned} 0 < \alpha \cdot \frac{x^m}{m} &\leq \frac{1}{\lambda} \int_0^x dx \int_0^x \frac{x^m}{m} dx \\ &= \frac{1}{\lambda} \frac{x^{m+2}}{m+2}, \end{aligned}$$

so that

$$\begin{aligned} \left| (\theta^4 \beta - p^2 \alpha) \cdot \frac{x^m}{m} \right| &\leq \frac{1}{\lambda} \frac{x^{m+2}}{m+2} \left( p^2 + \frac{\mu \theta^4 x^2}{(m+3)(m+4)} \right) \\ &< \nu^2 \cdot \frac{x^{m+2}}{m+2}. \end{aligned}$$



Hence

$$\begin{aligned} |(\theta^4\beta - p^2\alpha)^2\psi(x)| &\leq K\nu \left|(\theta^4\beta - p^2\alpha) \frac{x^2}{2}\right| \\ &< K\nu^2 \frac{x^4}{4}; \end{aligned}$$

$$\begin{aligned} |(\theta^4\beta - p^2\alpha)^3\psi(x)| &< K\nu^2 \left|(\theta^4\beta - p^2\alpha) \cdot \frac{x^4}{4}\right| \\ &< K\nu^3 \frac{x^6}{6}; \end{aligned}$$

and, generally,

$$\begin{aligned} \sum_{r=0}^{\infty} |(\theta^4\beta - p^2\alpha)^r\psi(x)| \\ < K \left[ 1 + \frac{\nu x^2}{2} + \frac{\nu^2 x^4}{4} + \dots \right], \end{aligned}$$

a series which is absolutely and uniformly convergent for all values of  $\nu$  and  $x$ .

Each of the series  $y$  is therefore absolutely and uniformly convergent. It follows easily that the series obtained by operating with

$$\theta^4 - p^2 \frac{d^2}{dx^2}$$

is uniformly convergent. For, if the first term is omitted the remainder may be written

$$\begin{aligned} \left(\theta^4 - p^2 \frac{d^2}{dx^2}\right)(\theta^4\beta - p^2\alpha)y \\ = \theta^4(\theta^4\beta - p^2\alpha)y + \frac{p^4}{\phi(x)}y - \frac{p^2\theta^4}{\phi(x)} \int_0^x dx \int_0^x dx f(x)y. \end{aligned}$$

The first two terms give series which are obviously uniformly convergent in view of the preceding discussion. Also, if  $R_N$  be the remainder after  $N$  terms of the series

$$\int_0^x dx \int_0^x dx f(x)y,$$

and  $R'_N$  the remainder in the series  $y$ , we can assign  $N$ , independently of  $x$ , so that

$$R'_N < \frac{\epsilon}{\mu},$$

where  $\mu$ , as before, is the upper bound of  $f(x)$  and  $\epsilon$  is

arbitrarily small. Then

$$\begin{aligned} R_N &< \frac{e}{\mu} \int_0^x dx \int_0^x f(x) dx \\ &< e \int_0^x dx \int_0^x dx = e \frac{x^2}{2} < e, \end{aligned}$$

so that the integrated series is also uniformly convergent, as is also the series

$$\left( \theta^4 - \rho^2 \frac{d^2}{dx^2} \right) y.$$

This justifies the procedure previously adopted and shows that the solution is valid for all values of the parameters.

The above argument needs a little modification when, as occurs in a later application, the shaft carries concentrated masses, since  $f(x)$  has then infinities in the range and no upper bound can be assigned to it. Suppose, for example, that  $f(x)$  has infinities at  $x = a_k$ ,  $k = 1, 2, 3, \dots$ , and that

$$\lim_{\epsilon \rightarrow 0} \int_{a_k - \epsilon}^{a_k + \epsilon} f(x) dx = \mu_k.$$

Then if  $\mu$  be the greatest value of  $f(x)$  in the intervals between the infinities and if  $\psi(x)$  be any continuous, bounded function,

$$\left| \int_0^x f(x) \psi(x) dx \right| \leq \mu \int_0^x |\psi(x)| dx + \sum |\mu_k| |\psi(a_k)|,$$

the summation extending to all values of  $a_k$  less than  $x$ . Writing

$$|\mu_1| |\psi(a_1)| = s_1,$$

$$|\mu_1| |\psi(a_1)| + |\mu_2| |\psi(a_2)| = s_2,$$

and so on, we have

$$0 < x < a_1 \quad \left| \int_0^x f(x) \psi(x) dx \right| \leq \mu \int_0^x |\psi(x)| dx,$$

$$a_1 < x < a_2 \quad \left| \int_0^x f(x) \psi(x) dx \right| \leq \mu \int_0^x |\psi(x)| dx + s_1,$$

$$\begin{aligned} a_i < x < a_{i+1} \quad \left| \int_0^x f(x) \psi(x) dx \right| &\leq \mu \int_0^x |\psi(x)| dx + s_i \\ &\leq \mu_i \int_0^x |\psi(x)| dx, \end{aligned}$$

$$\text{where} \quad \mu_i = \mu + \frac{s_i}{\int_0^{a_i} |\psi(x)| dx}.$$

Now let  $M$  be the greatest of the numbers  $\mu_1, \mu_2, \mu_3, \dots \mu_i, \dots$ . Then for every value of  $x$  in the range  $0 < x < 1$ ,

$$\left| \int_0^x f(x) \psi(x) dx \right| \leq M \int_0^x |\psi(x)| dx,$$

and  $M$  replaces  $\mu$  in the foregoing proof of convergence, which otherwise stands without change.

In the type of application that follows,  $p$  is regarded as known and the values of  $\theta$  are sought. For this purpose it is often convenient to rearrange the series in powers of  $\theta$ . The general solution of (10) then takes the form

$$y = Af_1(x) + Bf_2(x) + Cf_3(x) + Df_4(x), \quad (14)$$

where

$$\begin{aligned} f_n(x) = & y_n + \theta^4 [\beta - p^2(\beta\alpha + \alpha\beta) + p^4(\beta\alpha^2 + \alpha\beta\alpha + \alpha^2\beta) \\ & - \text{etc.}] y_n \\ & + \theta^8 [\beta^2 - p^2(\beta^2\alpha + \beta\alpha\beta + \alpha\beta^2) + \text{etc.}] y_n \\ & + \dots \text{ad inf.} \quad (15) \end{aligned}$$

and  $y_1, y_2, y_3, y_4$  have the values given in (13).

The solution is expressed entirely in terms of quadratures and is thus suited to graphical or numerical methods of calculation.

#### 4. Uniform Shaft Without Attached Masses.

When the shaft is uniform the integrations in (15) become very simple. Since an exact solution of (10) is also available in this case, a good opportunity is given for illustrating the accuracy of the present method and the types of error involved in truncating the series at different points.

When  $f(x) = \phi(x) = 1$ , the operators  $\alpha$  and  $\beta$  reduce to simple repeated integrations with regard to  $x$ . It will be convenient to have a special notation for such integrations. The following will be used:—

$$\left. \begin{aligned} S \psi(x) &\equiv \int_0^x \psi(x) dx, \\ S^2 \psi(x) &\equiv \int_0^x dx \int_0^x \psi(x) dx, \\ \text{and so on.} \\ S_1 \psi(x) &\equiv \int_0^1 \psi(x) dx, \\ S_1^2 \psi(x) &\equiv \int_0^1 dx \int_0^x \psi(x) dx, \\ \text{etc.} \end{aligned} \right\} \dots (16)$$

To avoid the use of additional brackets, it will be supposed that  $S$  operates upon all that follows it until a plus or minus sign is reached.

Then, in the problem considered, we have

$$y_1 = 1, \quad y_2 = S \cdot 1, \quad y_3 = S^2 \cdot 1, \quad y_4 = S^3 \cdot 1, \quad (17)$$

$$\alpha \equiv S^2, \quad \beta \equiv S^4,$$

and hence

$$\begin{aligned} f_n(x) = & y_n + \theta^4 [S^4 - 2p^2 S^6 + 3p^4 S^8 + \dots] y_n \\ & + \theta^8 [S^8 - 3p^2 S^{10} + 6p^4 S^{12} - \dots] y_n \\ & + \text{etc.} \end{aligned}$$

It is easily seen that this formula may also be written

$$f_n(x) = \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} (-1)^u \frac{u+v}{u!v!} p^{2u} \theta^{4v} S^{2u+4v} \cdot y_n. \quad (18)$$

So far, the result applies to any shaft of uniform flexural rigidity, whether the distribution of mass is uniform or not. When the functions  $y_n$  have the special values (17) the complete solution is

$$\left. \begin{aligned} y = & A f_1(x) + B f_2(x) + C f_3(x) + D f_4(x), \\ \text{where} \\ f_n(x) = & \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} (-1)^u \frac{u+v}{u!v!} \frac{x^{2u+4v+n-1}}{(2u+4v+n-1)!} p^{2u} \theta^{4v}. \end{aligned} \right\} \quad (19)$$

If the shaft has a short bearing at each end, the boundary conditions are

$$y = \frac{d^2 y}{dx^2} = 0, \text{ when } x = 0 \text{ or } 1. \quad (20)$$

From (19) it is obvious that

$$f_1(0) = 1, \quad f_2(0) = f_3(0) = f_4(0) = 0,$$

$$f_1''(0) = -p^2, \quad f_3''(0) = 1,$$

$$f_2''(0) = f_4''(0) = 0.$$

Hence

$$A = C = 0,$$

$$B f_2(1) + D f_4(1) = 0,$$

$$B f_2''(1) + D f_4''(1) = 0,$$

and the whirling speeds are given by

$$f_2(1) f_4''(1) = f_2''(1) f_4(1). \quad (21)$$

When the series in  $\theta$  is continued as far as the terms in  $\theta^8$  and the results are substituted in (21), an equation for  $\theta$  is obtained in the form

$$A\theta^4 = B + C\theta^8, \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where A, B, C have the values shown in Table I.

The Euler thrust at which the shaft tends to buckle when at rest is given by  $p^2 = \pi^2$ . In practice, the values of  $p^2$  which we have to consider will be much less than this and it will be found that powers of  $p$  above the sixth are negligible on account of the smallness of their coefficients. The calculation of A, B, and C is then very simple. Even when  $p^2$  is as great as 9 the convergence is rapid.

TABLE I.

	$p^2$ .	A.	B.	C.
Tension .....	-4	·01466	1·8134	$10\cdot55 \times 10^{-6}$
	-3	·01370	1·5806	$10\cdot09 \times 10^{-6}$
	-2	·01279	1·3683	$9\cdot65 \times 10^{-6}$
	-1	·01193	1·1752	$9\cdot23 \times 10^{-6}$
	0	·01111	1·0000	$8\cdot82 \times 10^{-6}$
Thrust.....	1	·01033	0·8415	$8\cdot42 \times 10^{-6}$
	2	·00961	0·6985	$8\cdot02 \times 10^{-6}$
	3	·00892	0·5699	$7\cdot68 \times 10^{-6}$
	4	·00827	0·4546	$7\cdot33 \times 10^{-6}$
	5	·00765	0·3518	$6\cdot99 \times 10^{-6}$
	7	·00653	0·1798	$6\cdot36 \times 10^{-6}$
	9	·00553	0·0470	$5\cdot78 \times 10^{-6}$

From (22) the lowest value of  $\theta^4$  may be found by successive approximation. Thus

$$\theta_0^4 = \frac{B}{A},$$

$$\theta_1^4 = \theta_0^4 + \frac{C}{A} \theta_0^8,$$

$$\theta_2^4 = \theta_0^4 + \frac{C}{A} \theta_0^8 + 2 \left( \frac{C}{A} \right)^2 \theta_0^{12},$$

$$\theta_3^4 = \theta_0^4 + \frac{C}{A} \theta_0^8 + 2 \left( \frac{C}{A} \right)^2 \theta_0^{12} + 5 \left( \frac{C}{A} \right)^3 \theta_0^{16}.$$

The values of  $\theta_0^4$ ,  $\theta_1^4$ , and  $\theta_3^4$  are given in Table II. Further approximation after  $\theta_3^4$  does not substantially alter the value

obtained and  $\theta_3^4$  may be taken as the final value of  $\theta^4$  given by (22).

TABLE II.

First, Second, and Final Approximations to  $\theta^4$ .

	$p^2$ .	$\theta_5^4$ .	$\theta_1^4$ .	$\theta_3^4$ .
Tension .....	-4	123.69	134.50	137.14
	-3	115.37	125.17	127.25
	-2	106.99	115.62	117.33
	-1	98.53	106.05	107.43
	0	90.00	96.43	97.50
Thrust .....	1	81.42	86.82	87.66
	2	72.69	77.11	77.79
	3	63.88	67.40	67.84
	4	54.99	57.67	57.96
	5	45.97	47.90	48.07
	7	27.54	28.28	28.33
	9	8.50	8.57	8.59

These results will now be compared with those given by the exact method. With the special values of  $f(x)$  and  $\phi(x)$  equation (5) becomes

$$\frac{d^4 y}{dx^4} + p^2 \frac{d^2 y}{dx^2} = \theta^4 y, \quad . \quad . \quad . \quad . \quad (23)$$

and the general solution is

$$y = A \cosh \alpha x + B \sinh \alpha x + C \cos \beta x + D \sin \beta x,$$

where

$$2\alpha^2 = \sqrt{p^4 + 4\theta^4} - p^2,$$

$$2\beta^2 = \sqrt{p^4 + 4\theta^4} + p^2.$$

The end conditions give

$$A = B = C = 0,$$

$$\text{and} \quad \sin \beta = 0.$$

From the last equation, the lowest whirling speed is to be found from

$$p^2 + \sqrt{p^4 + 4\theta^4} = 2\pi^2,$$

whence

$$\theta^4 = \pi^2(\pi^2 - p^2). \quad . \quad . \quad . \quad . \quad (24)$$

Table III. shows the values of  $\theta^4$  given by (24) and the errors in the approximations  $\theta_0^4$ ,  $\theta_1^4$ , and  $\theta_3^4$ .

TABLE III.

	$p^2$ .	$\pi^2(\pi^2 - p^2)$ .	Error in $\theta_0^4$ . per cent.	Error in $\theta_1^4$ . per cent.	Error in $\theta_3^4$ .
Tension .....	{ -4	136.89	9.5	1.93	{ Less than 0.2 per cent.
	{ -3	127.02	9.2	1.63	
	{ -2	117.15	8.8	1.46	
	{ -1	107.28	8.2	1.3	
	0	97.41	7.7	1.0	{ 0.1 per cent.
Thrust.....	{ 1	87.54	7.0	0.8	{ Less than 0.1 per cent.
	{ 2	77.67	6.4	0.7	
	{ 3	67.80	5.8	0.6	
	{ 4	57.93	5.1	0.5	
	{ 5	48.06	4.4	0.3	
	{ 7	8.32	22.7	0.1	
	{ 9	8.58	1.0	0.1	

Since in the case of whirling  $\theta^4$  contains  $\omega^2$  as a factor, the errors in  $\omega^2$  will be about half those in  $\theta^4$ . It will be seen that the errors in the first approximation are all less than 5 per cent. The errors in the second approximation are very small, while the final approximation gives  $\omega$  without appreciable error.

The inversion of Table II. by means of a graph will give the critical thrust at which the shaft tends to buckle when rotating with a given angular velocity and subjected to a forced vibration of given frequency.

Equation (22) may be solved also for the second value of  $\theta^4$ . This will be found too low by about 12 per cent., the error decreasing slightly as  $p$  increases. The value is corrected by including the  $\theta^{12}$  term in the equation. By extending the series further, we may calculate as many of the higher whirling speeds or higher frequencies as may be required.

### 5. Shaft Carrying Concentrated Masses.

If the shaft is uniform and of negligible mass but carries at intervals masses which may be regarded as particles, then in (12) we must put

$$\left. \begin{aligned} \phi(x) &= 1, \text{ everywhere;} \\ f(x) &= 0 \text{ except for } x = x_i, i = 1, 2, \dots, k; \\ \text{and } \lim_{\epsilon \rightarrow 0} \int_{x_i - \epsilon}^{x_i + \epsilon} f(x) dx &= \mu_i, \end{aligned} \right\} \quad (25)$$

where, if  $M_i$  is the attached mass,

$$\mu_i = \frac{M_i}{\rho A l}. \quad \dots \quad (26)$$

Then the required functions have the values :

$$\begin{aligned} f_2(x) = & x - \frac{p^2 x^3}{\underline{3}} + p^4 \frac{x^5}{\underline{5}} - \text{etc.} \\ & + \theta^4 \left[ S^4 x f(x) - p^2 \left\{ S^6 x f(x) + S^4 \frac{x^3}{\underline{3}} f(x) \right\} \right. \\ & \quad + p^4 \left\{ S^8 x f(x) + S^6 \frac{x^3}{\underline{3}} f(x) + S^4 \frac{x^5}{\underline{5}} f(x) \right\} \\ & \quad - p^6 \left\{ S^{10} x f(x) + S^8 \frac{x^3}{\underline{3}} f(x) + S^6 \frac{x^5}{\underline{5}} f(x) \right. \\ & \quad \quad \left. \left. + S^4 \frac{x^7}{\underline{7}} f(x) \right\} + \text{etc.} \right] \\ & + \theta^8 \left[ S^4 f(x) S^4 x f(x) - p^2 \left\{ S^6 f(x) S^4 x f(x) \right. \right. \\ & \quad \left. \left. + S^4 f(x) S^6 x f(x) + S^4 f(x) S^4 \frac{x^3}{\underline{3}} f(x) \right\} + \text{etc.} \right] \\ & - \text{etc.} \\ f_4(x) = & \frac{x^3}{\underline{3}} - p^2 \frac{x^5}{\underline{5}} + p^4 \frac{x^7}{\underline{7}} - \text{etc.} \\ & + \theta^4 \left[ S^4 \frac{x^3}{\underline{3}} f(x) - p^2 \left\{ S^6 \frac{x^3}{\underline{3}} f(x) + S^4 \frac{x^5}{\underline{5}} f(x) \right\} \right. \\ & \quad + p^4 \left\{ S^8 \frac{x^3}{\underline{3}} f(x) + S^6 \frac{x^5}{\underline{5}} f(x) + S^4 \frac{x^7}{\underline{7}} f(x) \right\} \\ & \quad - \text{etc.} \left. \right] \\ & + \theta^8 \left[ S^4 f(x) S^4 \frac{x^3}{\underline{3}} f(x) - p^2 \left\{ S^6 f(x) S^4 \frac{x^3}{\underline{3}} f(x) \right. \right. \\ & \quad \left. \left. + S^4 f(x) S^6 \frac{x^3}{\underline{3}} f(x) + S^4 f(x) S^4 \frac{x^5}{\underline{5}} f(x) \right\} + \text{etc.} \right] \\ & - \text{etc.} \quad \dots \quad (28) \end{aligned}$$



Now it is easily verified that

$$S^n \frac{x^r}{r} f(x) = \begin{cases} \frac{x < a_1.}{0} & \frac{x > a_1.}{+\mu_1 \frac{a_1^r}{r} \frac{(x-a_1)^{n-1}}{n-1}} & \frac{x > a_2.}{+\mu_2 \frac{a_2^r}{r} \frac{(x-a_2)^{n-1}}{n-1}} & + \text{etc.} \end{cases}$$

$$S^m f(x) S^n \frac{x^r}{r} f(x) = \begin{cases} \frac{x < a_2.}{0} & \frac{x > a_2.}{+\mu_1 \mu_2 \frac{(a_2-a_1)^{n-1}}{n-1} \frac{(x-a_2)^{m-1}}{m-1}} & \frac{x > a_3.}{+\mu_1 \mu_3 \frac{(a_3-a_1)^{n-1}}{n-1} \frac{(x-a_3)^{m-1}}{m-1}} & + \text{etc.} \\ & + \mu_2 \mu_3 \frac{(a_3-a_2)^{n-1}}{n-1} \frac{(x-a_3)^{m-1}}{m-1} & + \text{etc.} & + \text{etc.} \end{cases}$$

. . . (20)

Hence, writing  $1-a_i = b_i$

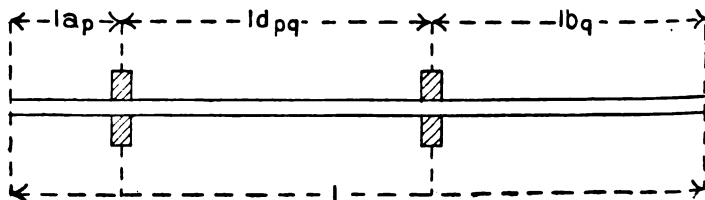
and  $1-a_p-b_q = d_{pq}$ , (fig. 2),

we have

$$\left. \begin{aligned} S_1^n \frac{x^r}{r} f(x) &= \sum_{i=1}^k \mu_i \frac{a_i^r}{r} \frac{b_i^{n-1}}{n-1}, \\ S_1^m f(x) S \frac{x^r}{r} f(x) &= \sum_{p,q=1}^k \mu_p \mu_q \frac{a_p^r}{r} \frac{d_{pq}^{n-1}}{n-1} \frac{b_q^{m-1}}{m-1}, \end{aligned} \right\} \quad (30)$$

where, in the last summation, each pair of masses is taken once only and  $p < q$ .

Fig. 2.



These give the following values of the functions in which, since the scope of each summation is obvious, the suffixes have been dropped :

$$\begin{aligned}
 f_1''(1) = & -p^3 + p^4 \frac{1}{\underline{3}} - p^6 \frac{1}{\underline{5}} + \text{etc.} \\
 & + \theta^4 \left[ \Sigma \mu a b - p^2 \Sigma \mu \left( a \frac{b^3}{\underline{3}} + \frac{a^3}{\underline{3}} b \right) \right. \\
 & \quad + p^4 \Sigma \mu \left( a \frac{b^5}{\underline{5}} + \frac{a^3}{\underline{3}} \frac{b^3}{\underline{3}} + \frac{a^5}{\underline{5}} b \right) \\
 & \quad \left. - p^6 \Sigma \mu \left( a \frac{b^7}{\underline{7}} + \frac{a^3}{\underline{3}} \frac{b^5}{\underline{5}} + \frac{a^5}{\underline{5}} \frac{b^3}{\underline{3}} + \frac{a^7}{\underline{7}} b \right) + \text{etc.} \right] \\
 & + \theta^8 \left[ \Sigma \mu \mu a \frac{d^3}{\underline{3}} b - p^2 \Sigma \mu \mu \left( a \frac{d^3}{\underline{3}} \frac{b^3}{\underline{3}} + a \frac{d^5}{\underline{5}} b + \frac{a^3}{\underline{3}} \frac{d^3}{\underline{3}} b \right) \right. \\
 & \quad + p^4 \Sigma \mu \mu \left( a \frac{d^3}{\underline{3}} \frac{b^5}{\underline{5}} + a \frac{d^5}{\underline{5}} \frac{b^3}{\underline{3}} + \frac{a^3}{\underline{3}} \frac{d^3}{\underline{3}} \frac{b^3}{\underline{3}} + a \frac{d^7}{\underline{7}} b \right. \\
 & \quad \left. \left. + \frac{a^3}{\underline{3}} \frac{d^5}{\underline{5}} b + \frac{a^5}{\underline{5}} \frac{d^3}{\underline{3}} b \right) - \text{etc.} \right],
 \end{aligned}$$

$$\begin{aligned}
 f_2(1) = & 1 - p^2 \frac{1}{\underline{3}} + p^4 \frac{1}{\underline{5}} - \text{etc.} \\
 & + \theta^4 \left[ \Sigma \mu a \frac{b^3}{\underline{3}} - p^2 \Sigma \mu \left( a \frac{b^5}{\underline{5}} + \frac{a^3}{\underline{3}} \frac{b^3}{\underline{3}} \right) \right. \\
 & \quad + p^4 \Sigma \mu \left( a \frac{b^7}{\underline{7}} + \frac{a^3}{\underline{3}} \frac{b^5}{\underline{5}} + \frac{a^5}{\underline{5}} \frac{b^3}{\underline{3}} \right) \\
 & \quad \left. - p^6 \Sigma \mu \left( a \frac{b^9}{\underline{9}} + \frac{a^3}{\underline{3}} \frac{b^7}{\underline{7}} + \frac{a^5}{\underline{5}} \frac{b^5}{\underline{5}} + \frac{a^7}{\underline{7}} \frac{b^3}{\underline{3}} \right) + \text{etc.} \right] \\
 & + \theta^8 \left[ \Sigma \mu \mu a \frac{d^3}{\underline{3}} \frac{b^3}{\underline{3}} \right. \\
 & \quad \left. - p^2 \Sigma \mu \mu \left( a \frac{d^3}{\underline{3}} \frac{b^5}{\underline{5}} + a \frac{d^5}{\underline{5}} \frac{b^3}{\underline{3}} + \frac{a^3}{\underline{3}} \frac{d^3}{\underline{3}} \frac{b^3}{\underline{3}} \right) + \text{etc.} \right].
 \end{aligned}$$

$$f_4''(1) = 1 - p^2 \frac{1}{\underline{3}} + p^4 \frac{1}{\underline{5}} - \text{etc.}$$

$$\begin{aligned}
 & + \theta^4 \left[ \Sigma \mu \frac{a^3}{\underline{3}} b - p^2 \Sigma \mu \left( \frac{a^3}{\underline{3}} \frac{b^3}{\underline{3}} + \frac{a^5}{\underline{5}} b \right) \right. \\
 & \quad + p^4 \Sigma \mu \left( \frac{a^3}{\underline{3}} \frac{b^5}{\underline{5}} + \frac{a^5}{\underline{5}} \frac{b^3}{\underline{3}} + \frac{a^7}{\underline{7}} b \right) \\
 & \quad \left. - p^6 \Sigma \mu \left( \frac{a^3}{\underline{3}} \frac{b^7}{\underline{7}} + \frac{a^5}{\underline{5}} \frac{b^5}{\underline{5}} + \frac{a^7}{\underline{7}} \frac{b^3}{\underline{3}} + \frac{a^9}{\underline{9}} b \right) + \text{etc.} \right] \\
 & + \theta^8 \left[ \Sigma \mu \mu \frac{a^3}{\underline{3}} \frac{d^3}{\underline{3}} b \right. \\
 & \quad \left. - p^2 \Sigma \mu \mu \left( \frac{a^3}{\underline{3}} \frac{d^3}{\underline{3}} \frac{b^3}{\underline{3}} + \frac{a^3}{\underline{3}} \frac{d^5}{\underline{5}} b + \frac{a^5}{\underline{5}} \frac{d^3}{\underline{3}} b \right) + \text{etc.} \right],
 \end{aligned}$$

$$f_4(1) = \frac{1}{\underline{3}} - p^2 \frac{1}{\underline{5}} + p^4 \frac{1}{\underline{7}} - \text{etc.}$$

$$\begin{aligned}
 & + \theta^4 \left[ \Sigma \mu \frac{a^3}{\underline{3}} \frac{b^3}{\underline{3}} - p^2 \Sigma \mu \left( \frac{a^3}{\underline{3}} \frac{b^5}{\underline{5}} + \frac{a^5}{\underline{5}} \frac{b^3}{\underline{3}} \right) \right. \\
 & \quad + p^4 \Sigma \mu \left( \frac{a^3}{\underline{3}} \frac{b^7}{\underline{7}} + \frac{a^5}{\underline{5}} \frac{b^5}{\underline{5}} + \frac{a^7}{\underline{7}} \frac{b^3}{\underline{3}} \right) \\
 & \quad \left. - p^6 \Sigma \mu \left( \frac{a^3}{\underline{3}} \frac{b^9}{\underline{9}} + \frac{a^5}{\underline{5}} \frac{b^7}{\underline{7}} + \frac{a^7}{\underline{7}} \frac{b^5}{\underline{5}} + \frac{a^9}{\underline{9}} \frac{b^3}{\underline{3}} \right) + \text{etc.} \right] \\
 & + \theta^8 \left[ \Sigma \mu \mu \frac{a^3}{\underline{3}} \frac{d^3}{\underline{3}} \frac{b^3}{\underline{3}} \right. \\
 & \quad \left. - p^2 \Sigma \mu \mu \left( \frac{a^3}{\underline{3}} \frac{d^3}{\underline{3}} \frac{b^5}{\underline{5}} + \frac{a^3}{\underline{3}} \frac{d^5}{\underline{5}} \frac{b^3}{\underline{3}} + \frac{a^5}{\underline{5}} \frac{d^3}{\underline{3}} \frac{b^3}{\underline{3}} \right) + \text{etc.} \right].
 \end{aligned}$$

. . . (31)

From these formulæ and equation (21), which applies equally in the present problem, an equation of the form

$$A\theta^4 = B + C\theta^8$$

may be obtained for each value of  $p$ . The neglect of the  $\theta^8$  term must lead, exactly as was shown for the shaft without end-thrust\*, to a formula equivalent, in the case of

\* *Loc. cit.* p. 1.

whirling, to Dunkerley's\*, while the  $\theta^8$  term gives a correction to the first approximation and allows the error in Dunkerley's rule to be estimated.

The calculation has been made for two, three, and five equal masses, equally spaced. Of the details of this work it is sufficient to mention:

(1) That the terms independent of  $\theta$  in the above series are expressible in terms of  $\sin p$  and may be calculated readily.

(2) That in the coefficients of  $\theta^4$  and  $\theta^8$  no more terms are needed than are shown above.

(3) That for symmetrically spaced loads,  $f_2''(1), f_4(1)$  are identical, while in the various summations many of the terms become equal in pairs.

Even with these simplifications, the calculation is laborious when values of  $p^2$  up to 9 are considered. When, however, as will generally be the case in practice,  $p$  is small, very few terms are needed for a reasonably accurate result.

The values of  $\mu\theta^4$  given by the first approximation (*i. e.* by Dunkerley's rule) are given in Table IV.; the corrected values obtained by including the  $\theta^8$  term are shown in Table V. In Table VI. are given the errors consequent on the use of Dunkerley's rule in each case. The results are given for four different values of the end-thrust and four of the tension, in addition to the zero value. The corrections for a uniform shaft are added for comparison.

TABLE IV.

Values of  $\mu\theta^4$  given by Dunkerley's Rule.

	$p^2$ .	2 masses.	3 masses.	5 masses.
Tension .....	-8	41.90	31.07	20.64
	-4	39.05	28.91	19.24
	-2	36.18	26.87	17.84
	-1	33.29	24.74	16.43
	0	30.38	22.59	15.00
Thrust.....	1	27.44	20.42	13.56
	2	24.49	18.23	12.14
	4	18.49	13.79	9.23
	8	6.10	4.62	3.07

\* Phil. Trans. A, clxxxv. (1894).

TABLE V.

Corrected Values of  $\mu\theta^4$ 

	$p^2$ .	2 masses.	3 masses.	5 masses.
Tension .....	-8	45.62	34.38	23.00
	-4	42.35	31.84	21.28
	-2	38.92	29.33	19.57
	-1	35.67	26.82	17.89
	0	32.38	24.37	16.32
Thrust.....	1	28.97	21.90	14.60
	2	25.74	19.41	12.97
	4	19.31	14.52	9.75
	8	6.21	4.72	3.14

TABLE VI

Errors in  $\omega$  as given by Dunkerley's Rule.

	$p^2$ .	2 masses. per cent.	3 masses. per cent.	5 masses. per cent.	Uniform Shaft. per cent.
Tension .....	-8	4.1	4.8	5.1	5.1
	-4	3.9	4.5	4.8	4.8
	-2	3.5	4.2	4.4	4.4
	-1	3.3	3.9	4.1	4.1
	0	3.1	3.6	3.8	3.8
Thrust.....	1	2.9	3.2	3.5	3.5
	2	2.5	3.1	3.2	3.2
	4	2.1	2.5	2.6	2.6
	8	0.9	1.0	1.0	1.0

All the errors have the same sign, the value of  $\omega$  given being consistently too low.

As the number of loads increases, the value of the error rapidly tends to the limiting value which it has for the uniform shaft. This limiting value decreases as the thrust increases.

Thus the error in Dunkerley's rule is greater for a shaft with tension and less for one with thrust than for a shaft without longitudinal stress. For moderate values of the stress the error is from 3.5 per cent. to 4 per cent. and is one of deficit.

I am indebted to Prof. L. N. G. Filon for valuable criticism and suggestions.

LVIII. *New Series in the Secondary Hydrogen Spectrum.* By  
W. E. CURTIS, D.Sc., A.R.C.S., Reader in Physics in the  
University of London, King's College\*.

**I**N view of the progress which is being made towards the solution of the problem of the analysis of the secondary hydrogen spectrum, it may be worth while to record several new series which I have recently found in this spectrum. They are only single branches, but if associated branches exist the particulars here given may assist workers in this field to discover them. In any case the spectrum is at present being studied under such widely varying conditions that evidence as to the genuineness or otherwise of the alleged series should not be long in appearing.

The first, denoted K, came to light during the examination of some work by Kimura and Nakamura† dealing with the influence of the electrodeless discharge on the secondary spectrum of hydrogen. They have given a list of some twenty lines which are enhanced under these conditions, and have pointed out several possible regularities amongst them. Of these, the only one which repaid further investigation was a sequence of four lines showing very small and almost constant second differences of wave-number. Reference to Merton and Barratt's tables gave two more members of the series on one side and a possible one on the other, making seven in all. The second differences are not quite constant, but increase so regularly that the reality of the series can hardly be doubted, especially when the intensity distribution and general properties of the lines are also taken into consideration.

Search was then made‡, using a graphical method, for other possible series in the same region and having first and second differences of the same order. Two were found, denoted G and H below, comprising six and five lines respectively. It was then noticed that four successive lines of G were included in Kimura and Nakamura's list; this circumstance, together with evidence derived from the properties, lends considerable support to the proposed arrangement. The credentials of H are hardly so good. There are only five lines, the middle one alone being recorded as strengthened by the electrodeless discharge,

\* Communicated by Prof. O. W. Richardson, F.R.S.

† Japanese Journ. Phys. vol. i. p. 86 (1923).

‡ By my wife.

although four of them are listed by Merton and Barratt as enhanced by a condensed discharge. The sensible constancy of the second differences cannot be regarded as decisive evidence, in view of the shortness of the series, but as a provisional arrangement it may be worthy of notice in future investigations.

In the table given below the columns headed L.P., H.P., C.D., and He are taken from Merton and Barratt's tables, and record the characteristics of the line as regards low pressure, high pressure, condensed discharge, and helium effect.

In column S the two lines marked — are noted by Sandeman \* as being much weakened in a discharge at atmospheric pressure as compared with an ordinary vacuum tube discharge.

Column R records the behaviour in Richardson and Tanaka's three types of discharge †.

Column K indicates the lines strengthened in the electrodeless discharge, as recorded by Kimura and Nakamura.

Column T gives the behaviour at a temperature of  $-252^{\circ}\text{C.}$ , according to the observations of McLennan and Shrum ‡.

Z indicates that a Zeeman effect has been observed. The present region is just outside the range of Dufour's results which are listed in Merton and Barratt, but is partially covered by an investigation of Croze §.

In cases where the line has already been allocated to a series, particulars are given in column X. The line marked F II is one of those added to Fulcher's second band by Allen ||. The remainder have been used by Richardson in various bands which he has recently published.

Series K may be regarded as well established, both on account of the very regular wave-number differences and of the similarity in behaviour of the lines with respect to temperature and the condensed discharge. But it is doubtful whether the first line, 16980, is really associated with the others, although the wave-number fits very well.

17426 figures as R(2) in Richardson and Tanaka's series no. 201 ¶, where however it is much too strong, and the authors suggest that there is a strong line superposed on

\* Roy. Soc. Proc. A, cviii. p. 607 (1925).

† Roy. Soc. Proc. A, cvi. p. 640 (1924). This information was kindly supplied to me by Prof. Richardson.

‡ Trans. Roy. Soc. Canada, xviii. p. 177 (1924).

§ *Ann. de Phys.* i. p. 63 (1914). No observations below 5760 Å.

|| Roy. Soc. Proc. A, cvi. p. 69 (1924).

¶ Roy. Soc. Proc. A, cvi. p. 663 (1924).

Series K.

$\lambda_{\text{air}}$	Int.	$\nu_{\text{vac}}$	H.P.	S.	L.P.	R.	C.D.	K.	T.	He	Z.	X.	1st diff.	2nd diff.	3rd diff.
5887.35	0	16980.87	+	...	-	...	-	...	...	+	Z	...	149.49	0.96	
35.98	9	17130.36	...	...	++	...	++	+	+	...	Z	...	148.53	0.21	
5785.81	7	278.89	...	...	++	I+	+	+	++	...	Z	...	147.36	1.17	0.13
36.88	8	426.25	...	-	...	...	+	+	++	...	...	201 R	146.06	1.30	0.20
5689.19	7	572.31	+	...	...	I-, II-	++	+	-	0	...	...	144.56	1.50	
42.78	3	716.87	...	...	...	II-	++	...	...	+	...	81 R	142.88	1.68	0.18
5597.63	4	859.75	...	...	++	...	+	...	+	...	...	...			

Series G.

5922.01	0	16881.52	...	...	++	...	++	...	...	...	Z	157 Q	144.30	1.01	
*5871.81	4	17125.82	...	...	++	...	++	...	++	...	Z	186 R	143.30	1.14	
22.80	5	169.12	...	...	++	...	++	+	+	...	Z	...	142.16	1.83	
*5774.98	7	311.28	...	...	++	...	++	+	+	...	Z	...	140.33	1.01	
28.54	7	451.61	+	-	...	II-	++	+	+	0	...	201 R	139.72		
5683.05	2	591.33	...	...	...	...	++	+	...	...	...	F II			

Series H.

5989.22	5	16892.04	++	...	...	I-	+	...	...	0	...	...	149.61	0.35	
36.02	4	841.65	...	...	...	...	...	...	...	...	...	...	149.26	0.74	
5883.88	6	900.91	++	...	...	II-, III-	++	+	...	...	...	...	148.52	0.70	
32.80	5	17130.43	...	...	...	...	++	...	...	...	...	...			
5783.01	2	287.25	...	...	...	...	++	...	...	+	...	...	147.82		

\* Unresolved doublets (M. & B.).



the real R(2). This is supported by Sandeman's observation that in the high-pressure discharge this line is much weakened in comparison with the remainder of the series (except 17451·61, *q. v.* below). It is thus probable that the K component of this line is of a low-pressure character, like the two preceding lines in the series.

17572 is exceptional in its pressure and temperature effects and may very well also be a blend.

17716 is claimed by Richardson and Tanaka \* as 81 R(7), but is a good deal stronger than their series seems to require and in their opinion may be "double, with constituents which are differentially affected by He."

Series G consists of only six lines, and the second differences show a slight irregularity which may be attributed to the observed duplicity of two of the lines. The properties are in good agreement except for 17451, but this is evidently due to the superposition of Richardson's 201 R(5), which being a high-pressure line masks the low-pressure character of the G line. This comes out clearly in Sandeman's observation at atmospheric pressure, where the intensity of this blend drops from 7 (M. & B., low pressure) to 3, bringing it into line with the rest of 201 R, evidently because the G constituent is suppressed. We conclude that the latter must be a low-pressure line, and it therefore agrees in this respect with the other three strong members of this series.

17025 coincides with Richardson's 157 Q(4)† and is noted as double by Merton and Barratt. It is difficult to estimate what intensity it should have in 157 Q, but since it is double it is permissible to claim one of the components for G.

17169 figures as 186 R(2)‡, where again the expected intensity is uncertain. But since 186 R has only five lines and less regular differences than G, the latter would appear to have at least as good a claim to it.

17591 has already been allocated to the second Fulcher band§, but seems a little too strong there. Its inclusion here is justified by its appearance in Kimura and Nakamura's list, where no other Fulcher line is to be found. But it is just possible that 17588 should be included instead.

Series H is somewhat problematical, but the differences are sufficiently regular to secure it some consideration. Also, four of its five lines are strengthened by the condensed discharge. None of them appear to have been already allocated to other series.

\* Roy. Soc. Proc. A, cvii. p. 617 (1925).

† Roy. Soc. Proc. A, cix. p. 240 (1925).

‡ *Id.* p. 239.

§ See Curtis, Roy. Soc. Proc. A, cvii. p. 573 (1925).

It is worthy of note that of the 18 lines, mostly strong ones, considered here, only one, 17859, is recorded\* as showing a Stark effect, although numerous other lines in this region (some 30 in all) are affected.

Five show a Zeeman effect, but our general acquaintance with the nature of this effect in band spectra has not yet progressed to the point where it is capable of providing definite evidence for or against the proposed arrangement. It may be observed, however, that band lines are susceptible to the Zeeman effect, which is sometimes of the "normal" order of magnitude and is of the same general character for lines belonging to the same branch.

It has not been possible to find any numerical relations between the three series, although their first and second differences are closely similar. K appears to be definitely of R type, but G and H might be either P or R branches. Search for associated branches on either side of this region has not led to any result. It is not likely that a Q branch exists, since the smallness of the second differences would give rise to a very small spacing in such a branch, and since also it should be intense there ought to be no difficulty in detecting it.

The moment of inertia of the molecule concerned in the emission of these bands is about  $3.7 \times 10^{-41}$  gm. cm.<sup>2</sup> and the change in its value due to the emission is hardly appreciable, being less than 1 per cent. This is unusual, in fact no other case is known in which the initial and final moments of inertia are so nearly equal. But since the emission process sometimes increases (band degraded towards the violet) and sometimes decreases (band degraded towards the red) the moment of inertia of the molecule, it is to be expected that cases may occasionally occur in which the change is practically nil.

*Later Note.*—I have recently availed myself of an opportunity (for which I have to thank Prof. Richardson) of examining one of Prof. Merton's plates of the secondary spectrum on which was also a comparison spectrum showing the "helium effect". Estimates were made of the intensities in each case, with the following results. The normal intensity is given first, *e.g.* 10, 2 means that the normal intensity 10 becomes 2 in presence of helium.

\* Kiuti, Japanese Journ. Phys. vol. i. p. 29 (1922).

No.	K Series.	G Series.	H Series.
1 .....	0, 0?	0, 0	5, 1
2 .....	10, 2	6, —	4, 4
3 .....	10, 2	7, 2+	6, 4
4 .....	9, 3	8+, 2+	6, 1
5 .....	7, 9	7-, 8	1, 2
6 .....	3, 3	1, —	
7 .....	4, —		

The striking similarity in the behaviour of K and G is strong evidence of the reality of both series. The distribution of the effect in the series is very like that in the Fulcher quintet at 6018 (the only one showing it clearly) where the fourth and fifth members are greatly strengthened by helium relative to the remainder (seen from the plate but not apparent from the tables, which do not indicate, either, the helium effects given above).

The observations do not support H in the same way, but this has throughout been regarded as a provisional arrangement, which would require confirmation before it could be accepted.

In addition, it was noted that K 6 is almost certainly double, since in helium it is appreciably displaced, suggesting that one component is suppressed. This supplements the evidence of duplicity previously put forward, viz. its allocation to Prof. Richardson's series 81 R.

In conclusion it may be observed that the object in view has been to give all the evidence concerning every line, even though it might not directly bear on the question as to whether the lines are associated. Since some of it is incomplete (*e.g.* Sandeman only examined one K line) and some difficult to interpret, the case for the alleged series must be regarded as resting mainly on the numerical relationships between the wave-numbers and the similarity of the electrical conditions favourable to the production of the lines.

### LIX. *Proceedings of Learned Societies.*

#### GEOLOGICAL SOCIETY.

[Continued from p. 560.]

November 4th, 1925.—Dr. J. W. Evans, C.B.E., F.R.S.,  
President, in the Chair.

THE following communications were read:—

1. 'Preliminary Notes on the Geology of the Eastern Parts of Central Spitsbergen: with especial reference to the Problem of the Hecla Hook Formation.' By Noel Ewart Odell, Assoc.R.S.M., F.G.S.

The region dealt with is that of New Friesland and Garwoodland, traversed by the inland sledging parties of the Oxford

University (Scientific) Expedition to Spitsbergen, 1921, and also by the Merton College (Oxford) Arctic Expedition, 1923.

Approximately, the area amounts to 2000 square miles, but only a relatively small portion of this could be actually examined. It consists of a mountainous tract much of which is submerged under 'highland ice' and glaciers, and is therefore lacking in direct rock-evidence. But through this ice-covering break many 'nunatakk', and on the west of the region a high range of mountains—the Chydenius Range—of which Mount Newton (5445 feet) is claimed to be the culminating point of Spitsbergen.

The rocks encountered include representatives of the Metamorphic Basement Complex, the Hecla Hook formation (which is intimately associated with that complex), the Carboniferous System, and intrusive acid and basic igneous facies.

The Metamorphic Complex and the Hecla Hook formation have long proved the chief enigma of Spitsbergen geology. The former, often designated the 'Urgebirge,' was long considered to be Archæan, and the latter (owing to complete lack of fossils throughout its great thickness) could not be dated. The relations of these two formations are rendered obscure by the intense folding and dislocation which they have suffered in most accessible areas.

There is an occurrence analogous to the Hecla Hook formation of Spitsbergen in Bear Island, situated half way between Spitsbergen and Norway, and this has been shown to be Ordovician in greater part, with a fauna of distinct American affinities.

The author found evidence in the extreme east of Spitsbergen, so much less highly disturbed than the west, of a lithological series of Hecla Hook rocks comparable with those described from Bear Island, although, with one possible exception, no unequivocal evidence of fossils could be obtained. Moreover, such sequences as were observed corresponded in general to those of Bear Island, although it would appear that in Spitsbergen there is exposed, in addition, a Lower Series of slates and massive quartzites of unknown thickness.

The whole formation in downward succession is as follows:—

**Upper Series.**

- (7) Cherty conglomerate.
- (6) Black and white chert-horizon.
- (5) Pale and dark dolomites and limestones of great thickness, often veined with calcite and dolomite, including an 'intra-dolomite conglomerate' present in Bear Island, and a fossil horizon of 'oolitoid' rock or 'ryssö-dolomite'.
- (4) Red shales, with thin quartzites and quartzose slates.

**Lower Series.**

- (3) Marbles and dark dolomitic limestones.
- (2) Dark shales, hard buff-coloured and blue slates weathering green, often spotted, and interbedded with pink quartzite.
- (1) 

<div style="display: inline-block; vertical-align: middle;">Purple massive quartzite Pink massive quartzite Yellow massive quartzite</div>	}	about 1000 feet exposed.
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The above succession must be considered as tentative only, since

the interrelationships of the members of the Lower Series in particular were very obscure, owing to dislocation and ice-covering. If, as is probable, No. 3 in the succession corresponds with Prof. O. Holtedahl's 'Ozarkian Stage' in the Bear Island sequence, then the lowest members are of Cambrian age.

A great north-and-south fault through the centre of the region is shown on A. G. Nathorst's map of 1910, but the existence of this was not confirmed. Instead, the line marks a zone of great stress, and the Hecla Hook formation here suffers its greatest metamorphism: interbedded with the highly altered sediments in this zone are intrusive rocks of granitoid and more basic affinities, the basic appearing the earlier.

No evidence was found of rocks earlier in age than the Hecla Hook Series, and an Archæan formation must be presumed absent.

The greatest acid intrusions are those of the pink and grey granites in the Mount Newton and Mount Chernishev massif. Evidence was obtained of the pre-Carboniferous (and presumably pre-Devonian) age of both these granites. They would appear to have been intruded at the time of the Caledonian folding, and though towards its close, yet prior to the earliest Devonian sedimentation.

Except in the south on the Nordenskiöld Glacier, where an erratic block of conglomerate was found, the Devonian strata are entirely absent from this region, having been eroded from the interfolded Hecla Hook sediments and granites before the transgression of the Upper Carboniferous sea. The Culm also is absent.

The Carboniferous, with its extensive dolerite-sills of Cretaceous age, has been much involved in the block-movements that resulted in the formation of the graben of Hinlopen Strait in Tertiary times, New Friesland correspondingly within that era being re-elevated as a horst.

The existing general geological maps of Spitsbergen, mostly based upon that of Nathorst (1910), indicate too great an areal extent of the Carboniferous. It was found to be confined more to the coast of Hinlopen Strait, from Cape Fanshawe as far south as Bismarck Strait. Moreover, Triassic deposits were not seen north of the latter, as opposed to their usual indication on the maps.

The Hecla Hook formation, with its highly metamorphosed components and associated intrusive suites, comprises, with the above-mentioned exceptions of Carboniferous and Triassic rocks, the whole region lying between Wijde Bay on the west and Hinlopen Strait on the east. It extends southwards to the neighbourhood of Sassen Bay on Ice Fiord; and it may be made to embrace the whole area variously indicated as 'Archæan' or 'Urgebirge' on the existing maps.

2. 'The Geology of North-East Land (Spitsbergen).' By Kenneth Stuart Sandford, M.A., D.Ph., F.G.S.

This paper is chiefly the result of exploration by the Oxford University Arctic Expedition of 1924. North-East Land is

separated by a narrow strait from the main island of Spitsbergen, and is about 8000 square miles in area. A great part of the coast and the whole of the interior are completely hidden by ice, which forms a dome rising to about 2400 feet. The paper attempts to show the geological history as deduced from such of the barren, ice-free outcrops as have been visited, and from a study of moraines.

North-East Land may be divided into two parts:—

Northern Area, consisting of Older Palæozoic rocks, granite, and gneiss: discussion arises as to the age of the last two, and the evidence, although not yet conclusive, in the author's opinion points to their being younger than the ancient sedimentary rocks: a pink granite penetrates the grey granite and gneiss, and has been found extensively developed in the southern part of this 'northern oldland.' An important discovery in 1924 was the south-eastern corner of the 'northern oldland' pink granite, in the middle of the east coast, which previously had been known only as an unbroken and precipitous ice-front over 100 miles long. The older Palæozoic—Hecla Hook formation—probably comprises the Cambrian to Silurian (from external evidence): it consists of unfossiliferous shales, quartzite, and dolerites to a very great thickness; there appears to be a general sequence over a wide area. Most of Spitsbergen was intensely affected by Caledonian folding and thrusting: the author has found in North-East Land the margin of this chain; the north-eastern part appears to be unfolded, while a narrow arc of intense disturbance affected part of the west coast, sending out ripples of rapidly decreasing magnitude. In Devonian times a vast thickness of deposits was formed in and over the Caledonian mountains: in North-East Land, however, only a trace (morainic material) of Devonian deposits has been found.

The Archipelago was next broken by block movement, and by the formation of broad graben and horsts: North-East Land appears to have been implicated. Of the Lower Carboniferous only uncertain traces have been found in moraines: the Middle Carboniferous is not exposed.

Southern Area, delimited from the northern by an east-and-west fjord. This is an area of undisturbed Upper Carboniferous and Permo-Carboniferous clays and cherts, to a visible thickness of more than 1000 feet: the fauna belongs to the Russian Province. A small area of Permian is known on the south-west coast, and is followed southwards by a few hundred feet of Trias. Close by, an island has been shown by Baron G. J. de Geer to consist of thin Jurassic beds (with coal) overlain by basalt (associated with dolerite; see below) and thin Cretaceous beds. The Jurassic sea extended south-south-westwards and eastwards to Franz Josef Land. North-East Land appears to have been implicated in extensive Lower Cretaceous base-levelling.

At this time enormous quantities of dolerite ascended along vertical fissures of definite trend from which originated basalt-flows, and dolerite-sills of great length and uniform thickness

(one 150 feet thick extending at least 40 miles). No Tertiary deposits have been found in North-East Land, and probably do not exist: they are well developed on the south-west (in Spitsbergen itself), where also there was strong folding in late Tertiary times along the Caledonian lines: North-East Land was unaffected.

The folding was followed by extensive fjord formation: on the west side of North-East Land the author finds especial significance in the coincidence of one set of fjords with the dolerite-fissures and a second set, destitute of dolerite, crossing them—at the crossing-point the maximum intrusion of dolerite occurred. The lines of weakness are, therefore, probably at least of Lower Cretaceous age. The Quaternary and recent history of North-East Land is not discussed in this paper.

The history of the island has been one of quiescence and immunity from folding, in an area of shallow seas. It has been affected by vertical movements, also by acid intrusions (Palæozoic) and by basic intrusions (Cretaceous).

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## LX. *Intelligence and Miscellaneous Articles.*

### THE WATER-SPARK ABSORPTION SPECTRUM OF IRON.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

IN a recent number of the Phil. Mag. (vol. i. p. 433, 1926) we find a very interesting article by Mr. N. K. Sur, "On the Water-Spark Absorption Spectrum of Iron." The author mentions the names of Wilsing, Hale, Konen, Victor Henri, Hulert, Angerer and Joos in connexion with this; and it would appear from this that he is not aware of our work "*Spéctres d'étincelle dans l'eau*" (*Le Journal de Physique et le Radium*, t. iii. d. 309, 1922). We may perhaps be permitted to remind him that this work embraces a detailed study of the water-spark absorption spectrum of Iron with a Table of the lines of absorption, which, commencing at a lower point and proceeding further than that of Mr. Sur, shows a considerably greater number of lines, and in the region common to both the lists practically coincide.

Yours faithfully,

LÉON BLOCH,  
EUGÈNE BLOCH.

Paris, February 13, 1926.

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[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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No. 4.—APRIL 1926.

WITH SIX PLATES.

Illustrative of Prof. F. H. NEWMAN's Paper on the Low Voltage Arc in Cæsium Vapour; Prof. F. H. NEWMAN's on Enhanced Lines produced by the Interrupted Arc in Sodium and Potassium Vapours; Dr. J. G. FRAYNE and Dr. A. W. SMITH's on the Absorption Spectra of the Vapours of Zn, Cd, Pb, Sn, Bi, and Sb; Mr. V. H. L. SEARLE's on the Wave Form of the Current in an Electrically Maintained Tuning-fork Circuit; Prof. J. K. ROBERTSON's on a Method for Exciting Spectra of Certain Metals; and Mr. R. N. GHOSH's on the Choice of Striking Point in the Pianoforte String.

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[SEVENTH SERIES.]

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APRIL 1926.

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LXI. *The Low Voltage Arc in Cæsium Vapour.* By  
F. H. NEWMAN, D.Sc., A.R.C.S., *Professor of Physics,*  
*University College of the South-West of England, Exeter* \*.

[Plate VIII.]

1. *Introduction.*

IN previous papers† it has been shown that the normal operation of an arc in sodium and potassium vapours results in the excitation of a line-by-line spectrum corresponding to changes of orbit involving less energy than the ionizing potential. The present work describes similar experiments that have been made with cæsium vapour.

Foote and Meggers‡, using a two-electrode discharge tube, photographed the cæsium spectrum at various accelerating voltages from  $\lambda$  3878 to  $\lambda$  9208 on dicyanin-stained plates. They found no evidence of group or single series spectra, but they proved the existence of a single-line spectrum— $\lambda$  8521,  $\lambda$  8943. This doublet was produced alone under excitation of 1.5 to 3.9 volts accelerating field, and the intensity of both of these lines gradually increased at a rate proportional to the total number of electrons reaching the anode until the ionization potential was reached; at this point there was a marked decrease in intensity of the lines. This decrease occurred at that voltage at which the complete

\* Communicated by the Author.

† Phil. Mag. l. p. 165 (1925) and l. p. 796 (1925).

‡ Phil. Mag. xl. p. 80 (1920).

spectrum was produced and can be explained on the basis of Bohr's theory of atomic structure. The lines of the doublet  $1\sigma-1\pi_{12}$  result from inelastic collisions with electrons possessing energy between 1.38 and 3.9 volts, but as the latter voltage is exceeded electrons which at a slightly lower voltage give rise to the lines  $1\sigma-1\pi_{12}$  now produce the complete series spectrum, and any line of the series  $1\sigma-m\pi$  is necessarily excited at the sacrifice of  $1\sigma-1\pi_{12}$ . These experimenters found that at voltages between 3.9, the ionizing potential, and 2.7, corresponding to  $1\sigma-2\pi$ , there was an emission of  $1\sigma-2\pi$ , *i. e.*,  $\lambda$  4593,  $\lambda$  4555, which could, however, be attributed to ionization. The electrons emitted by a heated cathode have a velocity distribution given by Maxwell's law, and even at a dull red heat a fraction of the electrons have a velocity 0.5 volt greater than the applied potential, so that the excitation of lines, other than  $\lambda$  8943,  $\lambda$  8521, below the ionization potential is explained by the small number of high velocity electrons present. So it was concluded that only two types of inelastic collision occur between electrons and atoms of caesium vapour, *viz.*, at the resonance and ionizing potentials respectively.

In view of this conflict between theory and experimental results, Hughes and Hagenow\* repeated the experiment with an apparatus which was essentially a three-electrode discharge tube having a nickel plate and grid. The caesium, obtained by heating a mixture of caesium chloride and caesium turnings, condensed on the surface of the nickel cathode and formed a very convenient thermionic source, yielding a copious supply of electrons below dull red heat. They found that the blue doublet,  $\lambda$  4555,  $\lambda$  4593, appeared with accelerating voltages between 2.8 and 3.0 volts, and the spectrograms showed satisfactory evidence of a step-by-step excitation, especially in the principal series; the results for the two subordinate series were not definite. No line in the latter series appeared at 3.5 volts, although they were all excited at 3.7-3.8 volts except  $\lambda$  6983,  $\lambda$  6973, for which the plate was probably insensitive.

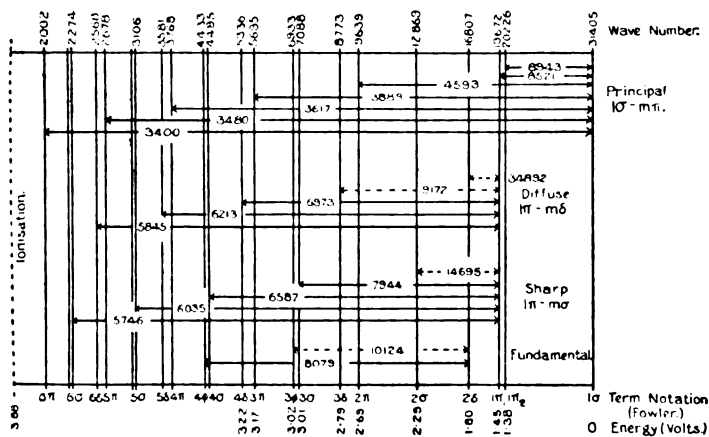
Theory indicates that the valence electron within the atom can be displaced from the normal orbit,  $1\sigma$ , directly to any  $m\pi$  orbit as a result of inelastic collision with the proper energy exchange, and as the probability of transfer from an  $m\pi$  orbit to the  $1\sigma$  orbit decreases rapidly as  $m$  increases, the probability of the displacement of the electron to an  $m\pi$  orbit as the result of electron-atomic collisions decreases as

\* Phys. Rev. xxiv. p. 229 (1924).

$m$  increases, even though all of the impacting electrons have energy corresponding to  $1\sigma - m\pi$ .

Considering the schematic representation of the cæsium atom shown in fig. 1, falls from the  $m\pi$  orbits to the normal orbit,  $1\sigma$ , give the principal series consisting of pairs with diminishing separation. Transfers from the  $\sigma$  and  $\delta$  rings to the two adjacent orbits, represented by  $1\pi_1$  and  $1\pi_2$ , yield the constant separation pairs of the sharp and diffuse series respectively; falls from the  $m\phi$  orbits to the orbit  $2\delta$  give the fundamental series consisting of single lines. The horizontal lines extending between orbits indicate the wave-length of the radiation emitted by energy falls between the

Fig. 1.



must possess to displace the valency electron to any orbit is denoted against that orbit. For example, 1.38 volts, indicated at the  $1\pi_2$  orbit, represents the impacting energy necessary to displace the electron from the  $1\sigma$  to the  $1\pi_2$  orbit, and radiation of  $\lambda 8943$  is emitted when the electron returns from the temporary to the stable orbit. Theoretically it should be possible to excite  $\lambda 8943$  without  $\lambda 8521$ , providing that the impacting energy lies within the range 1.38–1.45 volts, but in actual practice it would be difficult, if not impossible, to insure that no electrons in such a stream exceeded the higher limit of this energy range because of the distribution of velocities among the electrons emitted from an incandescent cathode. Colliding electrons of 2.69 volts energy should displace the valency electron to the  $2\pi$  orbit, and the second doublet of the principal series— $\lambda 4593$ ,  $\lambda 4555$ , should be excited when the displaced electrons return directly to the normal orbit. In addition to the direct return from the  $2\pi$  to the  $1\sigma$  orbit there is possible an indirect return from the  $2\pi$  to the  $1\pi_1$  and  $1\pi_2$  orbits, and from there to  $1\sigma$ , the latter step involving the emission of  $\lambda 8943$ ,  $\lambda 8521$ . The Bohr principle of selection shows that in the absence of a disturbing field a direct fall from  $2\pi$  to  $1\pi_1$  or  $1\pi_2$ , with the emission of  $2\pi-1\pi_1$ ,  $2\pi-1\pi_2$ , should not occur. The transition between these three orbits must be made through either the  $2\sigma$  or  $2\delta$  orbit as an intermediate stage. The lines excited at these intermediate stages,  $2\sigma-2\pi$ ,  $2\delta-2\pi$ , would not be observed, as they both lie far in the infra red. When caesium vapour is bombarded with electrons of energy 2.69 volts—corresponding to the  $2\pi$  orbit—radiation of  $\lambda 8943$ ,  $\lambda 8521$ ;  $\lambda 4593$ ,  $\lambda 4555$ ;  $\lambda 34892$ ,  $\lambda 30100$ ;  $\lambda 14695$ ,  $\lambda 13588$  should be excited by interorbital transfers permitted by the selection principle, in addition to the lines  $2\sigma-2\pi$  and  $2\delta-2\pi$ .

It should be noted that the valency electron returning to  $1\sigma$  from  $1\pi_1$  and  $1\pi_2$  and giving rise to  $\lambda 8943$ ,  $\lambda 8521$ , this radiation may be absorbed by any neighbouring caesium atoms, resulting in the ejection of the valency electron within these atoms to the  $1\pi_1$  and  $1\pi_2$  orbits. The excited or abnormal atoms thus formed may then be subjected to impacting energy of 2.69 volts, with the result that complete ionization is effected. Such a phenomenon is not likely to occur at low vapour pressures.

At present there is no evidence that the electron within the atom can be displaced to the  $m\delta$  or  $m\sigma$  orbits only by way of  $1\pi_1$  and  $1\pi_2$ . Klein and Rosseland\* have

\* *Zeit. f. Physik*, iv. 1, p. 46 (1921).

suggested that a slow-moving electron in collision with an excited atom may gain kinetic energy while the atom is assuming its normal state, no radiation being emitted in the process, so that collisions can occur between free electrons and atoms in which the atom bombarded passes without emitting radiation from a stationary state of greater energy into a stationary state of smaller energy, while the impacting electron acquires an amount of kinetic energy equal to the energy lost by the atom. This is the converse of excitation by collision. Franck \* has extended this idea to collisions between excited and unexcited atoms, and explains the appearance of the mercury line  $\lambda 2537-1S-1p_2$ , when mercury vapour is excited by  $\lambda 1849-1S-1P$ , by supposing a transition occurs without radiation from the  $1P$  orbit to the  $1p_2$  state.

## 2. Experiments.

A three-electrode discharge tube was used; the electrons emitted from a heated tungsten wire cathode were accelerated by a potential difference applied between the grid and the cathode, and entered a force-free space bounded by the grid and anode. Light from the immediate neighbourhood of the grid was focussed on the quartz spectrograph, and the spectra at various exciting potentials were photographed on dicyanin-stained plates. The whole of the discharge bulb, containing a small quantity of cæsium metal which had been distilled into the bulb from a side tube, was enclosed in an electric heater maintained at  $120^\circ C.$ , the vapour pressure of cæsium at this temperature being less than  $0.01$  mm. of mercury. The residual gas pressure was maintained below  $0.001$  mm. of mercury by means of an oil pump running continuously.

The electron currents were of the order of 2 milliamperes, and the discrepancy between the applied voltages and the potential actually used inside the discharge tube was determined, and allowed for, by measuring the ionization potential and comparing the value so obtained with the theoretical result, 3.88 volts.

As the accelerating voltage was raised from zero no visible radiation appeared until at 2.7 volts a blue glow appeared in close proximity to the grid and plate. This blue glow represents the excitation of the second doublet of the principal series,  $\lambda 4593$ ,  $\lambda 4555$ . Increasing the voltage still further, no change in the colour of the discharge

\* *Zeit. f. Physik*, ix. 5, p. 259 (1922).

was observed until at 3.9 volts the whole of the space between the grid and the plate was filled with a violet coloured radiation. From these results it is evident that the space charge lowers the effective potential except in the immediate neighbourhood of the grid and anode.

The spectrograms obtained at different voltages are shown in Plate VIII. In the first spectrogram the doublet  $\lambda$  8943,  $\lambda$  8521 appears at 1.6 volts, and is followed at 2.7 volts by  $\lambda$  4593,  $\lambda$  4555 as shown in the second spectrogram. The next lines to be excited should be  $\lambda$  9172,  $\lambda$  8761;  $\lambda$  7944,  $\lambda$  7609;  $\lambda$  3889,  $\lambda$  3876, respectively, but no additional lines appeared on the plate until the potential difference was raised to 3.2 volts, at which accelerating voltage  $\lambda$  7944,  $\lambda$  7609 and  $\lambda$  3889,  $\lambda$  3876 were photographed—Spectrogram III. It is probable that  $\lambda$  7944,  $\lambda$  7609 were excited below 3.2 volts, but the intensity of the radiation was so feeble that these lines were not registered on the plate, even though exposures of several hours duration were made. No additional lines were photographed until the ionization potential—3.9 volts—was reached, when the entire arc spectrum of cesium, as shown in the fourth spectrogram, was excited.

The various spectrum lines which appeared at different accelerating voltages are given in the following Table.

Series.	Wave-length.	Excitation voltage.	
		Experimental.	Calculated.
$\{ 1\sigma - 1\pi_2$	$\lambda$ 8943	1.6 volts.	1.38 volts.
$\{ 1\sigma - 1\pi_1$	$\lambda$ 8521	1.6	1.45
$1\pi_1 - 2\delta$	$\lambda$ 3489.2	—	1.80
$1\pi_1 - 2\sigma$	$\lambda$ 1469.5	—	2.29
$1\sigma - 2\pi$	$\lambda$ 4593	2.7	2.69
$1\pi_1 - 3\delta$	$\lambda$ 9172	—	2.79
$1\pi_1 - 3\sigma$	$\lambda$ 7944	3.2	3.01
$2\delta - 3\phi$	$\lambda$ 10124	—	3.02
$1\sigma - 3\pi$	$\lambda$ 3889	3.2	3.17
Complete arc spectrum		3.9	3.88

Although it was not possible to differentiate between the excitation of lines within the range 3.2–3.9 volts, probably

because the number of collisions resulting in excitation is small at the actual critical voltage, yet the evidence is in favour of a line-by-line excitation similar to that found with the other alkali metals.

The cost of the apparatus used in these experiments was defrayed by a Government grant, through the Royal Society, for which the author wishes to express his sincere thanks.

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LXII. *The Separation of the Modified and Unmodified Scattering Coefficients of X-Rays.* By G. E. M. JAUNCEY, D.Sc., Associate Professor of Physics, and O. K. DE FOE, M.Sc., Washington University, St. Louis, U.S.A. \*

### 1. Introduction.

THE Compton effect<sup>(1)</sup> necessitates a new experimental procedure when the scattering coefficient of X-rays in matter is measured. In fact, on account of the modified and unmodified X-rays produced by the scattering process, it becomes necessary to recognize two scattering coefficients—one for the modified and the other for the unmodified X-rays. What has previously been called the linear scattering coefficient  $\sigma$  is more correctly the sum of  $\sigma_1$ , the unmodified linear scattering coefficient, and  $\sigma_2$ , the modified linear scattering coefficient. In all previous experiments the calculation of  $\sigma$  has been based on the assumption that when homogeneous X-rays are scattered, the scattered X-rays have the same absorption coefficient as the primary rays in the scattering substance. The result of this assumption is that the calculated values of  $\sigma$ , or more correctly of  $\sigma_1 + \sigma_2$ , are all too small. However, due to the small change of absorption coefficient in the modified rays, the previously calculated values of  $\sigma$  are not far wrong.

Let us now distinguish between  $\sigma$  the spherical scattering coefficient, and  $s$  the linear scattering coefficient per unit solid angle in a direction  $\phi$  with the forward direction of the primary rays. For polarized rays  $s$  is a function of both  $\phi$  and of the angle between the electric vector of the primary rays and the plane of scattering. For our present purposes, however, we shall assume that the X-rays are

\* Communicated by the Authors.



unpolarized, so that  $s$  is a function of  $\phi$  only. In the experiments on scattering it is  $s$  which is first calculated from the experimental readings, and then  $\sigma$  is obtained from  $s$  by means of the formula

$$\sigma = \int_0^\pi 2\pi s \sin \phi \, d\phi. \quad . \quad . \quad . \quad . \quad (1)$$

In virtue of the Compton effect,  $s$ , like  $\sigma$ , consists of two parts— $s_1$ , the linear scattering coefficient per unit solid angle in the direction  $\phi$  for the unmodified rays, and  $s_2$ , a similar coefficient for the modified rays. The spherical coefficients  $\sigma_1$  and  $\sigma_2$  are related to  $s_1$  and  $s_2$  respectively by the formulæ

$$\sigma_1 = \int_0^\pi 2\pi s_1 \sin \phi \, d\phi, \quad . \quad . \quad . \quad . \quad (2)$$

and 
$$\sigma_2 = \int_0^\pi 2\pi s_2 \sin \phi \, d\phi. \quad . \quad . \quad . \quad . \quad (3)$$

## 2. Theoretical Considerations.

On Thomson's theory of scattering<sup>(3)</sup>  $s$  is given by

$$s = K(1 + \cos^2 \phi)/2, \quad . \quad . \quad . \quad . \quad (4)$$

and 
$$K = (NZ\rho/W) \cdot (e^4/m^2c^4), \quad . \quad . \quad . \quad . \quad (5)$$

where  $N$  is Avogadro's number,  $Z$  the number of electrons per molecule of the scattering substance,  $\rho$  its density and  $W$  its molecular weight,  $e$  and  $m$  the charge and mass of the electron, and  $c$  the velocity of light *in vacuo*. For convenience let us represent the value of  $s$  as calculated from the experimental readings on the assumption that there is no change of absorption coefficient on scattering by  $s_{\text{exp}}$ . It is found that when moderately soft X-rays are scattered by light elements,  $s_{\text{exp}}$  is very nearly given by Eq. (4) for values of  $\phi$  between about  $50^\circ$  and about  $120^\circ$ . However, even in this range  $s_{\text{exp}}$  shows a minimum at about  $100^\circ$  instead of at  $90^\circ$  as is required by the Thomson theory. For angles between about  $15^\circ$  and about  $50^\circ$  the phenomenon of scattering in excess of the Thomson amount, or excess scattering, is observed. For instance, a curve due to Barkla and Ayres<sup>(3)</sup> shows scattering of about twice the Thomson amount at  $20^\circ$ . The same effect has been observed by Hewlett<sup>(4)</sup>, Jauncey and May<sup>(5)</sup>, and others. At angles less than about  $15^\circ$  the scattering has been found by Hewlett, Jauncey and May, and others to fall quickly to zero. At

angles between about  $120^\circ$  and  $180^\circ$   $s_{\text{exp}}$  is less than the Thomson value and we have reduced scattering. The predictions of the Thomson theory are therefore only in approximate agreement with experimental fact for the scattering of moderately soft X-rays by light elements in the range  $50^\circ$  to  $120^\circ$ .

In 1923, A. H. Compton <sup>(1)</sup> and P. Debye <sup>(6)</sup> proposed a quantum theory of scattering which demands a change of wave-length on scattering. In addition, the angular distribution of the intensity of the scattered rays was worked out by A. H. Compton <sup>(1)</sup> and Jauncey <sup>(7)</sup>. The formula for  $s_2$  as given by these writers is

$$s_2 = \frac{K\{1 + \cos^2 \phi + 2a_0(1 + a_0) \text{vers}^2 \phi\}}{2(1 + a_0 \text{vers} \phi)^5}, \quad (6)$$

where  $a_0 = h/mc\lambda_0$  and  $\lambda_0$  is the wave-length of the primary rays. Eq. (6) is based on the assumption that the X-rays are scattered by free electrons originally at rest.

The values of  $s_2$  for the range  $50^\circ$  to  $180^\circ$  agree more closely with  $s_{\text{exp}}$  than do the Thomson values of  $s$ . On the other hand, the theoretical values of  $s_2$  do not agree at all with the excess scattering between  $15^\circ$  and  $50^\circ$  nor with the vanishing to zero of the scattering at angles less than  $15^\circ$ .

However, since the theoretical values of  $s_2$  are derived from the assumption of free electrons at rest it is not surprising that at the small angles there is considerable departure from theory, as on the quantum theory it is at these small angles that the energy given to the scattering electron becomes small, and therefore the electron cannot be ejected from the atom at these small angles. As experimental evidence that some of the scattering electrons are not ejected, may be cited the fact of the existence of unmodified scattering as shown by the experiments of Compton <sup>(2)</sup> and Ross <sup>(9)</sup>. On the theoretical side Jauncey has explained the existence of the unmodified scattering by taking into account the momentum and the binding energy of the scattering electrons. Jauncey's theory <sup>(10), (11)</sup> supposes that there is, for a given angle of scattering by a given type (K, L, etc.) of scattering electrons, a certain range of positions of the electron in its Bohr orbit from which the electron cannot be ejected by the scattering process, and that, in this case, the scattering takes place without change of wave-length. For positions outside of this range there is scattering with change of wave-length, although there is also a variation of this change of wave-length for a given

angle  $\phi$  depending on the position of the scattering electron in its orbit <sup>(10), (11), (12)</sup>. In other words, Jauncey's theory of the unmodified line requires that, of the  $NZ\rho/W$  electrons per unit volume of the scattering substance, there are at any instant of time  $pNZ\rho/W$  electrons which are in such orbital positions that if one of these electrons scatters a quantum in the direction  $\phi$  it will scatter with change of wave-length. If we consider the K electrons alone then the fraction  $p_K$  for the K electrons by Jauncey's theory is approximately given by

$$p_K = \frac{\alpha_0 \text{vers } \phi + 2 \sqrt{2\alpha_s} \sin \frac{1}{2}\phi - \lambda_0/\lambda_s}{4 \sqrt{2\alpha_s} \sin \frac{1}{2}\phi}, \quad . \quad . \quad (7)$$

where  $\alpha_s = h/mc\lambda_s$  and  $\lambda_s$  is the K critical absorption wavelength of the scattering substance. Similar formulæ hold for those L, M, etc. electrons which move in circular orbits, while more complicated formulæ exist for those electrons which are moving in elliptic orbits. Knowing the various fractions for the different kinds of electrons, it is an easy matter to obtain the average fraction for the whole atom. This we have denoted above by  $p$ , but since  $p$  is a function of  $\phi$  we shall henceforth represent it by  $p(\phi)$ . The theoretical value of  $s_2$ , instead of being given by Eq. (6) is now given by

$$s_2 = \frac{Kp(\phi) \{1 + \cos^2 \phi + 2\alpha_0(1 + \alpha_0) \text{vers}^2 \phi\}}{2(1 + \alpha_0 \text{vers } \phi)^5}, \quad . \quad (8)$$

provided that the motion of the scattering electrons in their Bohr orbits has no effect on the angular distribution of the intensity of the modified scattered rays.

The value of  $p(\phi)$  for the scattering of Mo K $\alpha$  X-rays from carbon is approximately unity for angles greater than  $75^\circ$ , and hence  $s_{\text{exp}}$  should agree fairly well with the theoretical values of  $s_2$  as given by Eq. (6), and this is found to be the case. However, for angles less than  $45^\circ$  the probability  $p(\phi)$  becomes less than unity decreasing to zero at  $5^\circ$ , which is the region where excess scattering exists. Hence, if our theory is correct, this excess scattering is connected in some way with the theoretical prediction that at angles less than  $45^\circ$  a large part of the scattered rays is of the unmodified type. That this prediction is at least in qualitative agreement with fact is shown by the experiments of Ross <sup>(13)</sup>, where he finds no modified line, or at least a modified line of very small intensity, relative to that of the unmodified line when Mo K $\alpha$  X-rays are scattered at  $30^\circ$  by copper. Further support of the suggested connexion between excess scattering

and unmodified scattering is given by the fact that  $s_{\text{exp}}$  for copper is found by Barkla and White<sup>(14)</sup> to be greater than the Thomson value at  $90^\circ$ , and that the excess scattering becomes greater as the primary rays become softer. This is in accord with our theory, as  $p(\phi)$  becomes less as the atomic weight of the scattering substance becomes greater and also as the wave-length becomes longer. Still further support of our idea is given by Compton's values for  $s_{\text{exp}}$  for the scattering of gamma rays. In Compton's paper<sup>(1)</sup> a curve is given showing how closely  $s_{\text{exp}}$  for gamma rays agrees with  $s_2$ , as given by Eq. (6), for the range  $30^\circ$  to  $180^\circ$ . For gamma rays  $p(\phi)$  is very nearly unity at  $30^\circ$ , and hence the agreement.

In Jauncey's papers<sup>(10), (11)</sup> an expression is derived for the ratio of the energy of the modified to that of the unmodified rays scattered at a certain angle. The derivation, however, is based on the assumption that the energy scattered in a given direction  $\phi$  is the same whether the scattering electron is scattering modified or unmodified rays. We do not feel, however, that this is necessarily so. In fact our experiments, so far, indicate that the energy in the unmodified rays is a greater fraction of the total energy in the modified and unmodified rays in a direction  $\phi$  than is predicted by Jauncey's expression. It is our present idea that although the angular distribution of modified energy is given by Eq. (8), yet the angular distribution of unmodified energy is not necessarily given by replacing the factor  $p(\phi)$  by the factor  $\{1 - p(\phi)\}$  in Eq. (8).

From the previous remarks in this section it is therefore obvious that it is very necessary to devise a method, or methods, of measuring both  $s_1$  and  $s_2$  experimentally in order to test our theory.

### *3. Theory of the Experimental Methods.*

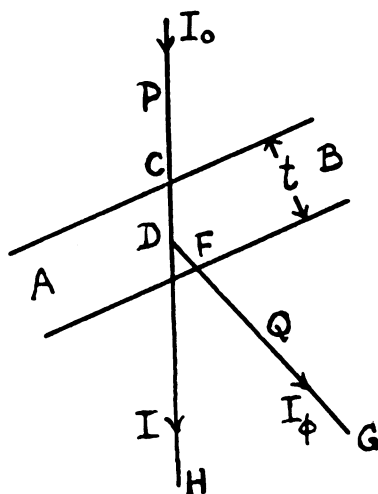
In both of the methods to be described a known thickness of absorbing material is transferred from a position where the primary X-rays pass through this material to a position where the scattered rays in a certain direction pass through the material before entering the ionization chamber. The first position we shall denote as the P position, and the second as the Q position. If all of the scattered rays in a certain direction  $\phi$  are of the unmodified type, the intensity of the rays entering the ionization chamber will be unaltered by transferring the absorbing material from P to Q, provided that the intensity of the primary rays remains constant. However, if part of

the scattered rays are modified, part of the primary rays of wave-length  $\lambda_0$  will be changed to rays of wave-length  $\lambda_\phi$ , where  $\lambda_\phi$  is given by the Compton equation <sup>(1)</sup>

$$\lambda_\phi - \lambda_0 = (h/mc) \text{ vers } \phi. \quad . \quad . \quad . \quad (9)$$

If we know  $\lambda_0$  we can determine the absorption coefficient of the primary rays in the absorbing material by reference to a curve of absorption coefficients plotted against wave-length. Now making use of Eq. (9) we can, from the same curve, determine the absorption coefficient of the modified rays scattered in the direction  $\phi$  in the absorbing material, or better still, the change of absorption coefficient on scattering. The intensity of the rays entering the ionization chamber when the absorbing material is at P is greater than when it is at Q, and the difference between the intensities when the absorbing material is at P and that when it is at Q is a function of the fraction of modified rays present in the scattered beam.

Fig. 1.



*Method 1.*—This method is a modification of Crowther's method <sup>(15)</sup>. A beam of primary X-rays of intensity  $I_0$  passes first through a thickness  $T_1$  of absorbing material (in our experiments we use aluminium) placed at P and then falls upon a slab of scattering substance AB (fig. 1). The intensity of the primary rays arriving at D is therefore  $I_0 e^{-(\mu_1 T_1 + \mu_2 x)}$ , where  $\mu_1$  and  $\mu_2$  are the linear absorption coefficients of the primary rays of wave-length  $\lambda_0$  (the primary rays are

supposed homogeneous) in the absorbing material and scattering substance respectively, and  $x=CD$ . The intensity of the modified rays scattered by an element  $dx$  at D per unit solid angle in the direction  $\phi$  is  $s_2 I_0 e^{-(\mu_1 T_1 + \mu_2 x)} dx$ . These scattered rays traverse a distance DF in the scattering substance. The scattered rays then pass through a thickness R of air and a thickness  $T_2$  of the absorbing material placed at Q and then enter the ionization chamber. If  $\mu_3$ ,  $\mu_4$  and  $\mu_6$  are the linear absorption coefficients of the modified scattered rays in the absorbing material, the scattering substance and air respectively, and A is the area of the ionization chamber window, the intensity of the modified rays entering the chamber is

$$(dI_\phi)_{\text{mod}} = \frac{A s_2 I_0 e^{-(\mu_1 T_1 + \mu_2 T_2 + \mu_3 x + \mu_4 y + \mu_6 R)}}{R^2} dx, \quad (10)$$

where  $y=DF$ , the distance R being great compared with  $T_2$  and the thickness of the scattering slab. For the unmodified rays the intensity entering the ionization chamber window is

$$(dI_\phi)_{\text{unmod}} = \frac{A s_1 I_0 e^{-(\mu_1 T_1 + \mu_1 T_2 + \mu_3 x + \mu_3 y + \mu_6 R)}}{R^2} dx, \quad (11)$$

where  $\mu_6$  is the absorption coefficient of unmodified rays in air.

As in Crowther's method, the normal to a face of the scattering slab AB makes an angle  $\phi/2$  with the direction of the primary rays. We then have  $DF = (t \sec \frac{1}{2}\phi - x)$ , where  $t$  is the thickness of the scattering slab. The chamber is now swung around to H so as to receive the primary rays while the absorbing material which was at Q is now placed so that the primary rays pass through it. The intensity of the primary rays entering the chamber is I, where

$$I = I_0 e^{-(\mu_1 T_1 + \mu_1 T_2 + \mu_3 t \sec \theta + \mu_6 R)}, \quad (12)$$

where  $\theta = \phi/2$ .

Eqs. (10) and (11) are added, obtaining  $(dI_\phi)_{\text{total}}$ . This last named quantity is then integrated from  $x=0$  to  $x=t \sec \theta$ , and making use of Eq. (12) we obtain

$$I_\phi = CI \{ s_1 + s_2 e^{-(kT_2 + b)} (e^g - 1) / g \}, \quad (13)$$

where

$$C = At \sec \theta / R^2$$

$$k = (\mu_2 - \mu_1)$$

$$b = (\mu_6 - \mu_6) R + g$$

$$g = (\mu_4 - \mu_3) t \sec \theta$$

and

$$\left. \begin{array}{l} C = At \sec \theta / R^2 \\ k = (\mu_2 - \mu_1) \\ b = (\mu_6 - \mu_6) R + g \\ g = (\mu_4 - \mu_3) t \sec \theta \end{array} \right\} \quad (13 A)$$

In order to obtain  $s_1$  and  $s_2$  it is necessary to determine

the values of  $I_\phi$  for two values of  $T_2$ , the thickness of the absorbing material in the scattered beam. However, in order to keep  $I$  constant it is necessary to keep  $(T_1 + T_2)$  constant, even though  $T_2$  is varied. This is accomplished by transferring a certain thickness  $d$  of the absorbing material from  $P$  to  $Q$  in fig. 1. Let  $i_1$  and  $i_2$  be the values of  $I_\phi$  when  $T_2$  has the values  $d_1$  and  $d_2$  respectively. We then find

$$s_2 = \frac{g(i_1 - i_2)}{CI(e^g - 1)e^{-(kd_1 + b)}(1 - e^{-kd})}, \quad \dots \quad (14)$$

and 
$$s_1 = \frac{i_2 - i_1 e^{-kd}}{CI(1 - e^{-kd})}, \quad \dots \quad (15)$$

where  $d = (d_2 - d_1)$ , the thickness of aluminium transferred from  $P$  to  $Q$  between the readings of  $i_1$  and  $i_2$ . It is seen that the ratio of  $s_1$  to  $s_2$  can be obtained from Eqs. (14) and (15) provided that  $I$ , and therefore  $I_0$ , remains constant without a knowledge of  $I$ .

However, instead of measuring  $I_\phi$  for two different values of  $T_2$  when  $I$  (or  $I_0$ ) is kept constant, we may keep  $I_\phi$  constant by varying  $I$  (or  $I_0$ ).

Let  $I_1$  be the value of  $I$  (or  $I_0$ ) when  $T_2$  has the value  $d_1$  and  $I_2$  the value of  $I$  when  $T_2$  has the value  $d_2$ , then we obtain

$$\frac{s_2}{s_1} = \frac{g(I_2 - I_1)}{(eg - 1)e^{-(kd_1 + b)} \cdot (I_1 - I_2 e^{-kd})}. \quad \dots \quad (16)$$

*Method II.*—In this method the slab of scattering material is set with the normal to a face of the slab bisecting the angle  $PDQ$ , as shown in fig. 2.

As in Method I. there is a thickness  $T_1$  of absorbing material in the primary beam at  $P$  and a thickness  $T_2$  of the same material at  $Q$ . In this case we suppose the slab to be so thick that no primary rays get through it as in Crowther's method, and we therefore integrate from  $x=0$  to  $x=\infty$  in obtaining  $I_\phi$ . The formula of Eq. (13) is now replaced by

$$I_\phi = DI_0 \{s_1 + Bs_2 e^{-kT_2}\}, \quad \dots \quad (17)$$

where 
$$\left. \begin{aligned} D &= A/(2R^2\mu_3) \\ B &= e^{-kR}/\{1 + (\mu_4 - \mu_3)/2\mu_3\} \end{aligned} \right\} \quad \dots \quad (17A)$$

and 
$$h = \mu_6 - \mu_5$$

As in Method I. we may keep  $I_0$  constant and measure the two values  $i_1$  and  $i_2$  of  $I_\phi$  when we have the two values  $d_1$  and  $d_2$  of the thickness  $T_2$ ; or we may keep  $I_\phi$  constant and measure the two values  $I_1$  and  $I_2$  of  $I_0$  when we have the

values  $d_1$  and  $d_2$  of the thickness  $T_2$ . In the former case <sup>(18)</sup>

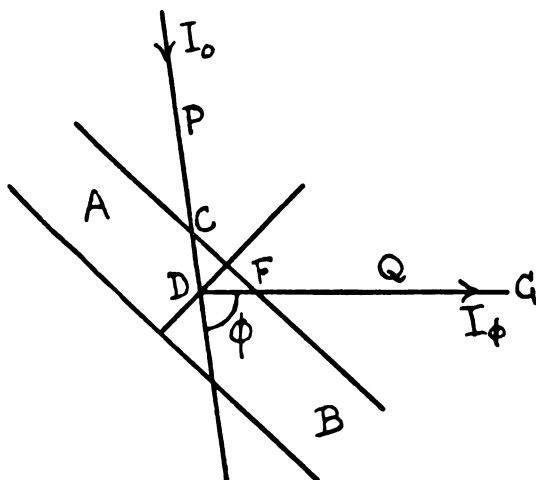
$$s_1 = \frac{i_2 - i_1 e^{-kd}}{DI_0(1 - e^{-kd})}, \quad \dots \quad (18)$$

and

$$s_2 = \frac{i_1 - i_2}{DBI_0 e^{-kd_1}(1 - e^{-kd})}, \quad \dots \quad (19)$$

where  $d = (d_2 - d_1)$ , the thickness transferred from P to Q.

Fig. 2.



In the latter case

$$\frac{s_2}{s_1} = \frac{I_2 - I_1}{Be^{-kd_1}(I_1 - I_2 e^{-kd})} \cdot \dots \quad (20)$$

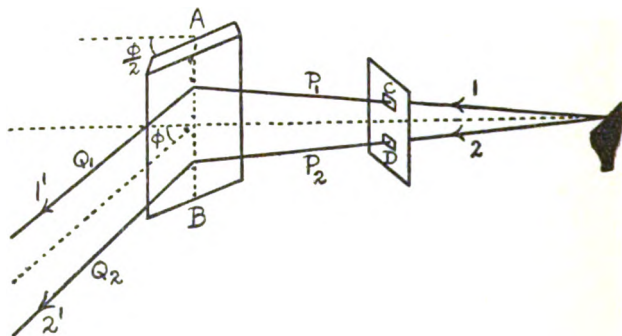
#### 4. Experimental Arrangement.

Eqs. (16) and (20) suggest the use of a balance method for determining the ratio  $s_2/s_1$ . We have used Method II. and Eq. (20) for determining the ratio for copper as the scattering substance. Fig. 3 represents our experimental arrangement. Two primary beams 1 and 2, after passing through two slits C and D and thence through absorbing material placed at P<sub>1</sub> and P<sub>2</sub>, fall upon the scattering block AB. From AB scattered beams 1' and 2' proceed through absorbing material at Q<sub>1</sub> and Q<sub>2</sub> and thence to two ionization



chambers. The inner electrodes of these two chambers are connected to the same electrometer, while the outer electrodes are connected to opposite potentials, so that if the intensities of the two scattered beams are the same the deflexion of the electrometer is zero. In our experiments the same thickness of aluminium is placed at  $P_1$  as at  $P_2$ , while the thickness at  $Q_1$  is the same as at  $Q_2$ . The opening of the slit at D is kept constant, while that of the slit at C is varied by means of a micrometer screw until the electrometer shows no deflexion and the reading of the micrometer recorded. A thickness  $d$  of aluminium is now transferred from  $P_1$  to  $Q_1$ , no

Fig. 3.



aluminium, however, being transferred from  $P_2$  to  $Q_2$ . The effect of this is that the intensity of beam 1' entering the upper ionization chamber is less than that of beam 2' entering the lower chamber. Hence, in order to bring back the balance it is necessary to open the slit at C and its micrometer reading is again observed. These two micrometer readings then replace  $I_1$  and  $I_2$  in Eq. (20). In order to find  $k$  in Eq. (20) it is necessary to know the wave-length of X-rays. This we have determined by placing sufficient additional aluminium at  $P_1$  to double the width of the slit at C. From this added thickness we calculate the average wave-length of the primary rays.

To determine the absolute values of  $s_1$  and  $s_2$  we use Crowther's experimental method and calculate  $s_1$  and  $s_2$  from Eq. (13), since we already know the ratio  $s_2/s_1$ .

Our experimental results will be reserved for another paper, which we hope will appear in the near future.

References.

- (1) A. H. Compton, *Phys. Rev.* **xxi.** p. 483 (1923).
- (2) J. J. Thomson, 'Conduction of Electricity through Gases,' 2nd Ed., p. 325.
- (3) Barkla and Ayres, *Phil. Mag.* **xxi.** p. 275 (1911).
- (4) C. W. Hewlett, *Phys. Rev.* **xx.** p. 688 (1922).
- (5) Jauncey and May, *Phys. Rev.* **xxiii.** p. 128 (1924).
- (6) P. Debye, *Phys. Zeit.* **xxiv.** p. 161 (1923).
- (7) G. E. M. Jauncey, *Phys. Rev.* **xxii.** p. 233 (1923).
- (8) A. H. Compton, *Phys. Rev.* **xxii.** p. 408 (1923).
- (9) P. A. Ross, *Proc. Nat. Acad. Sci.* **x.** p. 304 (1924).
- (10) G. E. M. Jauncey, *Phys. Rev.* **xxv.** p. 314 (1925).
- (11) G. E. M. Jauncey, *Phys. Rev.* **xxv.** p. 723 (1925).
- (12) G. E. M. Jauncey, *Phil. Mag.* **xlix.** p. 427 (1925).
- (13) P. A. Ross, *Am. Phys. Soc. Meeting*, Dec. 29-31, 1924.
- (14) Barkla and White, *Phil. Mag.* **xxxiv.** p. 275 (1917).
- (15) J. A. Crowther, *Proc. Roy. Soc.* **lxxxvi.** p. 478 (1912).
- (16) A brief announcement of Eqs. (14), (15), (18) and (19) is given by De Foe and Jauncey in *Proc. Nat. Acad. Sci.* **xi.** p. 517 (1925).

Washington University.  
St. Louis, Mo., U.S.A.  
October 23, 1925.

**LXIII.** *Enhanced Lines produced by the Interrupted Arc in Sodium and Potassium Vapours.* By F. H. NEWMAN, D.Sc., A.R.C.S., Professor of Physics, University College of the South-West of England, Exeter\*.

[Plate IX.]

1. Introduction.

IT is well known that although the enhanced lines of various metals occur chiefly in the spark discharge, some appear in the arc burning between metallic electrodes, particularly at that part of the arc in the vicinity of the poles†. The emission of enhanced lines under these conditions has been attributed to the high potential gradient at the electrodes, which results in the electrons at these regions attaining impacting energy sufficient to eject the second electron from the atom. It has been found by Crew‡, and by Fowler and Payne§, that the spark lines in the arc become prominent in the presence of hydrogen,

\* Communicated by the Author.

† Duffield, *Astrophys. Jour.* **xxvii.** p. 260 (1908). Fabry and Buisson, *Jour. d. Phys.* **ix.** p. 929 (1910).

‡ *Astrophys. Jour.* **xii.** p. 167 (1900).

§ *Proc. Roy. Soc. A*, **lxxii.** p. 253 (1903).

although in general this gas does not seem to be essential for the excitation of such lines.

An exhaustive study of the occurrence of these lines in the arc discharge has been made by Hemsalech and de Gramont\*, who used an arc passing between a metal, placed on a copper plate, and a pointed carbon rod which, fixed vertically above the metal, could be raised or lowered as desired. They found that the spark lines flashed into prominence in the arc discharge as the degree of ionization was lowered, which was brought about, for example, by blowing air across the arc. The lines disappeared when the carbon rod, acting as the cathode, became white hot, but were intensified by cooling the electrodes to  $-190^{\circ}\text{C}$ . by immersion in liquid air. They also attained a high degree of development if a drop of liquid which offered a comparatively high resistance was placed between the poles before starting the arc. This excitation of the enhanced lines in this liquid film arc was independent of the nature of the liquid, provided that the distance between the electrodes did not exceed 0.1–0.5 mm. At greater distances the liquid film was destroyed, and a second phase of the arc followed in which a transitory flash passed between the electrodes. During this second phase the spark lines showed feebly. In one particular experiment it was estimated that with 80 volts applied between the electrodes the end of the first phase occurred when they were 0.05 mm. apart, the electric field at this point being 16,000 volts per cm. Such a high electric force is maintained only so long as no discharge passes. Directly the arc is established the electric force decreases rapidly. The existence of this initial intense electric field seemed to be confirmed by the broadening of the  $\text{H}_{\alpha}$  and  $\text{H}_{\beta}$  hydrogen lines, observed during the early stages of the arc flash.

Hemsalech and de Gramont point out that the emission of light radiation in the arc is governed by a number of factors which generally act simultaneously, and thereby complicate the task of tracing the origin of any particular spectrum lines; but, in general, the existence of strong electric fields seems to be directly responsible for the emission of enhanced lines. These experimenters explain the “flashing up” of the lines, at the moment of striking the arc in various gaseous atmospheres, by suggesting that as the upper electrode in their experiments moves away from the stationary one a vacuous space is formed, momentarily, between the electrodes, and the initial stages of the arc discharge take

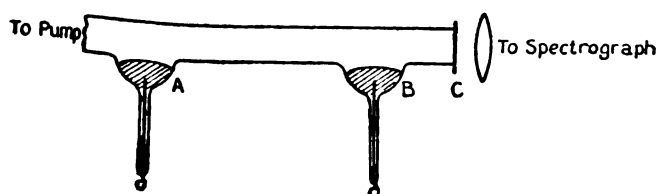
\* Phil. Mag. xliii. p. 287 (1922).

place through this space. In this manner the electric field set up is enabled to develop its effect before any appreciable chemical action starts between the vapours and the surrounding gas.

Lowery\*, using gold, silver and copper arcs under conditions similar to those of Hemsalech and de Gramont, found that in addition to the enhanced lines of these metals, which appeared during the initial stages of the arc flash, other lines were present which had not been observed previously. He also noted a distinct widening of the lines in the silver arc spectrum at the region near the fixed pole where, presumably, the electric fields are very intense during the early stages of the arc.

While working with the sodium-potassium alloy vapour arc lamp, which the author has described previously†, it was noticed that after the arc had been burning for some time and was then quenched, it could be restarted immediately after the cessation by applying a potential difference across the electrodes without any preliminary heating and without bringing the two liquid electrodes into momentary contact, which must be done to start the ordinary mercury vapour arc. This phenomenon can be explained by supposing the electrons and metastable atoms to persist within the lamp for an appreciable time interval after the arc had been

Fig. 1.



extinguished. It was observed, also, that the arc restarted in this manner gave an emission spectrum which was at first different from that emitted by the steady continuously burning arc. A preliminary investigation of the phenomenon was made with a type of lamp shown in fig. 1.

## 2. Experiments.

The alloy electrodes, A, B, were about 8 cm. apart; one end of the silica tube was closed by a quartz plate C, and

\* Phil. Mag. xviii. p. 1122 (1924).

† Phil. Mag. xlv. p. 944 (1922).

the other end was connected to an oil pump which, running continuously, maintained the residual gas pressure below  $10^{-3}$  mm. Radiation from the tube was focused by means of a quartz lens on the slit of a quartz spectrograph, and it is important to notice that in no case was the radiation from the immediate neighbourhood of either electrode incident on the spectrograph. The arc was started by warming the tube by means of a bunsen flame and passing a momentary electrodeless discharge through the vapour. After the arc had been burning for a few minutes it was stopped, and transient arc flashes produced in the tube by a mercury make and break arranged in the external circuit. In addition to this make and break the external circuit consisted of a wire rheostat, ammeter and accumulators, so that the self inductance in the circuit was very small. The applied potential difference was 80 volts, the current being 1 ampere. Arc flashes could be produced in this manner for a considerable period provided that the interval between successive flashes did not exceed 5–10 seconds.

The spectrum of these flashes differs considerably from that emitted by the steady burning arc in which, as shown in spectrogram No. I., Pl. IX., the predominant radiation is the first doublet of the principal series of sodium,  $\lambda$  5890,  $\lambda$  5896, the intensity of the D-lines being so great that the plate is fogged in this part of the spectrum. The lines of the two subordinate series of sodium are prominent, particularly those of the diffuse series. In the spectrum of the intermittent arc—spectrogram No. II.—the principal series lines of sodium and potassium are faint, and the subordinate series lines of sodium are almost entirely absent. The corresponding potassium lines are present and although comparatively feeble are more intense than the sodium lines. The complicated enhanced line spectra of the two metals predominate.

This characteristic spark spectrum from the intermittent arc resembles that obtained from an electric discharge tube in which one electrode was a pool of the alloy and the other an iron wire having some of the alloy coated on the end. When an electric discharge passed, very brilliant radiation was emitted from the end of the iron wire. The spectrum of this light—spectrogram No. III.—is similar to that shown in spectrogram No. II.

The spectrum of the radiation emitted from the intermittent arc at high vapour pressures is given in spectrogram No. IV., and is intermediate in character between that excited by the steady and intermittent arcs at low vapour

pressures. In addition, there is a continuous spectrum which extends to  $\lambda 2100$ .

It may be mentioned that although the applied potential was 80 volts, this dropped to 15 volts when the arc was burning steadily, and it seems evident that the "flashing up" of the enhanced lines is explained by the relatively high potential fall which operates when the arc is started. The potential gradient in the neighbourhood of the electrodes is high, and the electrons in these parts may acquire impacting energy between successive atomic collisions sufficient to doubly ionize sodium and potassium atoms, thus giving rise to the enhanced lines.

It has been pointed out by Foote, Meggers and Mohler \*, that the critical impacting energy necessary for the excitation of the enhanced lines of sodium is about 30 volts, while for potassium it is about 20 volts, but such energies are unlikely to be acquired by the bombarding electrons from the electric field except, perhaps, at the electrodes. As pointed out previously, it was not the radiation from either electrode that was focussed on the spectrograph, but light from the axial portion of the tube. Under these circumstances it is unlikely that the double ionization is effected directly by impacting energy, but it is brought about by some cumulative action. The electrons themselves acquire energy from the radiating atoms. Such collisions can occur between free electrons and atoms, in which the atom bombarded passes without emitting radiation from a stationary state of greater energy into a stationary state of smaller energy, while the impacting electron acquires an amount of kinetic energy equal to the energy lost by the atom.

Another controlling factor in the excitation of the enhanced lines in the flash arc spectrum is the phenomenon of absorption of that radiation which is emitted when the atoms resume their normal conditions. This radiation may be absorbed by any neighbouring atoms, resulting in the ejection of the electrons to temporary orbits. The excited atom thus formed may then collide with another impacting electron, which singly ionizes the atom. The radiation emitted in the first instance is probably diffused throughout the vapour in all directions, and this "photo-impact" ionization is relatively of far greater importance, especially at high vapour pressures, than ionization by successive impacts.

\* *Astrophys. Journ.* lv. p. 145 (1922).

In the immediate vicinity of the electrodes the potential fall is high, and the electrons at this part of the arc may possess that impacting energy necessary to displace the second electron within the sodium or potassium atom. The enhanced line radiation thus produced then diffuses throughout the vapour in all directions, and is absorbed by atoms along the length of the tube. Double ionization in these excited atoms may then be completed by bombarding electrons of energy far below the theoretical values.

LXIV. *Refractivity, Ionization Potentials, and Absorption Spectra.* By R. A. MORTON, *Ph.D.*, and R. W. RIDING, *Ph.D.\**

THE classical theory leads to a dispersion formula of the Lorenz-Lorentz type:—

$$\frac{n^2 - 1}{n^2 + 2} = \frac{C}{\nu_0^2 - \nu^2} + \frac{C'}{\nu_0'^2 - \nu^2} + \frac{C''}{\nu_0''^2 - \nu^2} + \dots \quad (1)$$

where  $n$  is the refractive index for light of the frequency  $\nu$ ,  $\nu_0$ ,  $\nu'$ ,  $\nu''$ , etc. are natural vibration frequencies of the absorbing entity, and  $C$ ,  $C'$ ,  $C''$ , etc. are constants. In gases and vapours  $n$  is practically unity, and a single term dispersion formula gives a close approximation to experimental results. Thus (1) reduces to

$$2/3 \cdot n - 1 = C/(\nu_0^2 - \nu^2). \quad (2)$$

Expressed otherwise,

$$n - 1 = \frac{e^2 N}{2\pi m} \cdot \frac{1}{\nu_0^2 - \nu^2}, \quad (3)$$

where  $N$  is the number of electrons per cubic centimetre which are effective in dispersion. In the form

$$n - 1 = \frac{N'}{\nu_0^2 - \nu^2} \quad (4)$$

it is known as the Sellmeier dispersion formula.

The expression accounts for the observed dispersion of many gases†. This fact leads us to inquire into the physical significance of the frequency term  $\nu_0$ . On the classical theory it should correspond to a natural vibration

\* Communicated by Professor E. C. Baly, F.R.S.

† Cuthbertson, *Proc. Roy. Soc. A*, vol. lxxx. p. 411 (1908), and several later papers; Burton, *ibid.* p. 390; Koch, *Ark. f. Mat.* ix. p. 611 (1913).

frequency of the refracting entity, or in other words we should find a large absorption of radiation of the frequency  $\nu_0$ . Unfortunately, the observations lead to frequencies on the short-wave side of 1200 Å., a region only amenable to investigation by means of vacuum spectroscopy. Further, the most transparent substance known, namely fluorite, ceases to transmit light below 1200 Å.

Attempts to verify the deduction that  $\nu_0$  corresponds in its physical significance with the head of an absorption band are thus bound to be very difficult. A beginning has been made by Hopfield and others by filling the entire vacuum spectrograph with gases at very low pressures. It is, however, uncertain how much significance can rightly be attached to such results from the special point of view we are considering.

Workers in the field of vacuum spectroscopy are familiar with the difficulty that the discharge is liable to spread throughout the entire apparatus. The absorption spectrum in the extreme ultra-violet is determined by illuminating the gas with a wide range of frequencies under conditions whereby excitation is not precluded, whereas the refractivity is measured for monochromatic light, using the unexcited gas. There is therefore some doubt as to the validity of attempts at correlating  $\nu_0$  with absorption measured in this way. We therefore propose to search for a substance whose dispersion may be expressed by a single- or double-term classical expression leading to the prediction of an absorption band on the long-wave side of 1200 Å. The correlation can then be subjected to a rigorous test by investigating the absorption spectrum of the gas or vapour contained in a cell with fluorite windows. In this way the absorbing layer may be isolated from the electrical discharge of the light source, and excitation may be avoided. The present work embodies the results of some preliminary calculations.

Another line of argument may be discussed. The well-known quantum relation  $h \cdot c/\lambda = V$  enables us to express wave-lengths in terms of voltage. Expressed more conveniently,

$$\lambda(\mu) = 1.234/V,$$

e. g. the mercury line 2537 Å. =  $0.254 \mu = 1.234/4.9$  volts. It is obvious that the  $\nu_0$  terms of the Sellmeier expressions are important natural frequencies, and it would be interesting to see whether the related voltages correspond with observed voltage discontinuities. This had been done when it was discovered that we had been anticipated\*. It is somewhat

\* Hershfeld and Wolf, *Ann. d. Physik*, lxxvi. pp. 71-106 (1925).



startling that the calculated voltages correspond quite accurately with ionization potentials.

For the monatomic gases,  $\nu_0$  in Cuthbertson's data on helium corresponds with 507.2 Å., and the corresponding voltage is 24.33. The observed ionization potential is 24.5. For neon there is a wide discrepancy, 25.6 volts (calc.) as against 21.5 volts (obs.). For argon the values are 16.97 and 17.0 respectively. For krypton the values are 14.7 and 13.3 and for xenon 12.34 and 10.86 volts \*.

Herzfeld and Wolf (*loc. cit.*) have investigated the effect of using a two-term formula :

$$n - 1 = C' / (\nu_{\text{res.}}^2 - \nu^2) + C'' / (\nu_{\text{ion.}}^2 - \nu^2), \quad . \quad . \quad (5)$$

where  $\nu_{\text{res.}}$  and  $\nu_{\text{ion.}}$  are frequencies corresponding with resonance and ionization potentials. They come to the very interesting conclusion that the added resonance term leads to a degree of agreement with experiment which is no better and no worse than when the simple expression is used. The observations on voltage discontinuities are liable to considerable errors, so that  $\nu_{\text{res.}}$  and  $\nu_{\text{ion.}}$  must also be inaccurate. The formula is sensitive to small alterations in these terms, so that it is not surprising to find only moderately good reproduction of very accurate refractivity data. It would seem to be better to begin from refractivity and end with voltages.

These conditions also affect the work of Bergen Davis †. This author observed ‡ that the simple theory leads to a value of  $\nu_0$  for hydrogen corresponding with a potential of 16.4, which agrees fairly well with observed ionization potentials (16.0 and 16.9 volts). He then extended the formula by inserting other terms with additional  $\nu_0$  frequencies, corresponding with voltages characteristic of energy changes at levels other than the first. Some of his results may be summarized as follows :—

Substance .....	C.	N.	O.	S.	Cl.	Br	I.
Voltages observed... }	11.5 35	17 29.9	15.5 52	12.2 35	13.2 46	11.3 32.6 10	21
Voltages assumed in calculation. }	15 35	17 29.9	18.5 25	12.2 16.2	13.2 35.3	11.3 25.8 10	13.8

\* Ionization Data : Hertz, *Z. Physik*, xxviii. p. 207 (1923) ; Barton, *Nature*, cxiv. p. 826 (1924) ; Hertz, *Z. Physik*, xxxi. p. 470, and xxxii. p. 933 (1925).

† *Phys. Rev.* xxvi. p. 232 (1925).

‡ The simple Sellmeier expression of Cuthbertson, *Proc. Roy. Soc. A*, lxxxiii. p. 166 (1910), does not lead to 16.4 volts but 14.5 volts.

It will be observed that only in one case, that of nitrogen, are the calculated and observed voltages in agreement. The work of Herzfeld and Wolf in finding that the introduction of a second term into the dispersion formula neither improves nor worsens the degree of agreement would seem to militate against the work of Davis, and would still do so even if his calculated and observed voltages were in agreement. Davis himself writes that in the cases of helium, neon, and argon the observed potentials do not give the refractive indices if any reasonable distribution of electrons is assumed.

We have calculated the ionization potentials for the following gases from Cuthbertson's refractivity data :—

Substance.	" Dispersion " band.	$V_{(ion.)}$ calc.	$V_{(ion.)}$ obs.
Nitrogen.....	725.5 Å.	17.01	17.0; 16.9; 16.3; 16.2
Hydrogen .....	851.8 „	14.5	15.8; 16; 15.8; 16.9 *
Oxygen .....	838 „	14.72	$\left. \begin{smallmatrix} 12.5 \\ 16.1 \end{smallmatrix} \right\}$ ; 15.5; 14.0; 15.5
Carbon monoxide .....	899 „	13.72	$\left. \begin{smallmatrix} 14.1 \\ 15.6 \end{smallmatrix} \right\}$ ; 14.3; 14.5; 15.1
Nitric oxide .....	859 „	14.3	9.3
Ammonia .....	1052 „	11.7	11.1
Carbon dioxide .....	800 „	15.04	14.3
Hydrogen sulphide ...	1070 „	11.3	10.4

\* Richardson and Tanaka, Proc. Roy. Soc. A, cvi, pp. 640-662 (1924), give the value 14.5 volts.

The moderate agreement implies the need for a second term in the equation.

This need is emphasized by the work of Koch (*loc. cit.*). He extended the dispersion data of various gases into the ultra-violet, and although he expressed his results by means of the Cauchy formula his conclusions are relevant. With the exception of helium, the assumption of only one fundamental ultra-violet period does not account for the course of the dispersion data. The deviations are especially great in carbon monoxide and nitric oxide, in which strong additional ultra-violet absorption is found. We have seen that the employment of resonance and other potentials by Herzfeld and Wolf and by Davis does not materially assist the discussion. The development of satisfactory two-term formulæ must, therefore, apparently wait on extended data of absorption spectra in the vacuum region.

One other possibility remains to be explored, namely, the influence of absorption bands in the near ultra-violet.

The case of chlorine at once suggests itself, because of the very accurately measured absorption band in this region.

Cuthbertson's data are formulated by the expression

$$n-1 = 7.3131 \cdot 10^{27} / (9629.4 \cdot 10^{27} - \nu^2),$$

and  $\nu_0$  corresponds with 967 Å. or 12.7 volts. The observed value for the ionization potential is 13.2 volts. Mr. and Mrs. Cuthbertson themselves recognized the necessity for a second term in the equation. In order to explain how a two-term formula has been devised, it is necessary to turn to work in a quite different field.

Baly\* has advanced a theory of absorption spectra which is conveniently described as centring round the molecular phase hypothesis. This hypothesis regards the natural frequencies of an absorbing entity as integral multiples of a fundamental frequency situated in the short-wave infra-red region. Accordingly (if the hypothesis is valid) any two frequencies entering into dispersion formulæ should be integral multiples of a common frequency. Hence Baly† has proposed what we shall call the Baly-Sellmeier formula:

$$\begin{aligned} (n-1)(V_1 + V_2 + V_3 + \dots) \\ = \frac{V_1 N_1}{(a\nu_x)^2 - \nu^2} + \frac{V_2 N_2}{(b\nu_x)^2 - \nu^2} + \frac{V_3 N_3}{(c\nu_x)^2 - \nu^2} + \dots, \end{aligned}$$

where  $\nu_x$  is an infra-red frequency,  $a$ ,  $b$ , and  $c$  are integers,  $a\nu_x$ ,  $b\nu_x$ ,  $c\nu_x$  are those frequencies which affect dispersion.  $V_1$ ,  $V_2$ ,  $V_3 \dots$  are the relative volumes of the absorbing entities exhibiting the frequencies  $a\nu_x$ ,  $b\nu_x$ ,  $c\nu_x$  respectively. and  $N_1$ ,  $N_2$ ,  $N_3 \dots$  are constants.

For chlorine, the experimental data on dispersion are reproduced extremely accurately by

$$n-1 \cdot 350.6 = \frac{5.98548 \cdot 10^{26}}{7.873996 \cdot 10^{29} - \nu^2} + \frac{349.6 \cdot 7.96606 \cdot 10^{27}}{104.79487 \cdot 10^{29} - \nu^2}.$$

The central wave-length of the first band is 3380.8 Å. (observed 3380 Å.) and the second band is at  $\nu = 32.37 \cdot 10^{14}$

\* Phil. Mag. xl. p. 15 (1920).

† Baly and Morton, Journ. Phys. Chem. xxviii. p. 659 (1924).

or. 926 Å., which corresponds with 13.3 volts. Hence the observed potential of 13.2 volts is well reproduced. The expression was derived from refractivity data only, and the assumptions of the phase theory are not essential from the special point of view of this paper. The essential fact is that an equation has been arrived at which

- (a) very accurately reproduces the data ;
- (b) employs the frequency of an accurately measured absorption band in the near ultra-violet ;
- (c) leads to a frequency in the extreme ultra-violet which is very much closer to the value calculated from the ionization potential than that obtained from the simple dispersion formula.

This result leads us to place some reliance on the correlation of ionization potential with a dispersional frequency. It also seems to justify an attempt to measure absorption spectra in the region 1200–1800 Å. with a view to confirming these views.

It may be asked why the dispersional frequency should be related in any way to the ionization potential. Except that both phenomena are concerned with outer electrons, no answer can be made. The dispersion equations are of classical origin, whereas the conversion of voltages into frequencies is made by quantum assumptions, so that the reconciliation of the wave theory and the quantum theory is somehow involved.

It would also seem that if with photoactivation of chlorine there is a concomitant change in physical properties, the illumination of chlorine with ultra-violet light to as far as  $\lambda=1200$  Å. (using a fluorite window) should result in a change of refractive index large enough to be measured interferometrically.

We express our thanks to the United Alkali Company, who, by the most generous terms of appointment, have enabled one of us (R. W. R.) to undertake experimental work on the above lines for one year at the University of Liverpool.

LXV. *The Absorption Spectra of the Vapours of Zn, Cd, Pb, Sn, Bi, and Sb.* By JOHN G. FRAYNE, *Ph.D.*, and ALPHEUS W. SMITH, *Ph.D.*\*

[Plate X.]

**I**N a recent paper by Zumstein † a new kind of absorption cell is described. The cell is a graphite tube open at both ends, the bead of metal under observation being placed in the centre of the tube. An oxy-acetylene torch is used to vapourize the metal. All previous absorption cells have had quartz windows at both ends in order to allow the ultra-violet light to pass through, at the same time making it possible to evacuate the apparatus. The deposition of the metal on the windows was a serious handicap in this type of apparatus. Further, it was impossible to heat such a cell above  $1150^{\circ}\text{C.}$ , the softening point of fused quartz.

The present research was undertaken by the authors to test the feasibility of using this new type of cell for metals of low melting points. Cadmium was first investigated and gave positive results on the first spectrogram. Wood and Guthrie ‡ had previously investigated the absorption spectrum of this element and had found two heavy absorption lines. Absorption in zinc vapour has been studied by McLennan and Edwards §. Grottrian || has made a study of absorption in lead vapour, finding twelve lines in the ultra-violet. While this research was in progress, Zumstein ¶ published a paper on lead absorption in which he states that thirty lines were absorbed in the ultra-violet. McLennan, Young and McLay\*\* have studied the absorption spectrum of tin. They used the evacuated quartz tube and arc reversal methods. Grottrian †† has found the line  $\lambda 3067$  strongly absorbed in Bi vapour and also found band absorption at high temperatures. Ruark, Mohler, Foot and Chenault ‡‡ have studied the emission and absorption spectra of metals in Group V. of the Periodic

\* Communicated by the Authors.

† Zumstein, *Phys. Rev.* xxv. p. 523 (1925).

‡ Wood and Guthrie, *Astrophys. Journ.* xxix. p. 211 (1909).

§ McLennan and Edwards, *Phil. Mag.* xxx. p. 695 (1915).

|| Grottrian, *Zeit. fur Phys.* xviii. p. 169 (1923).

¶ Zumstein, *Phys. Rev.* xxvi. p. 189 (1925).

\*\* McLennan, Young and McLay, *Trans. Roy. Soc. Can.* xviii. p. 57 (1924).

†† Grottrian, *Zeit. fur Phys.* xviii. p. 169 (1923).

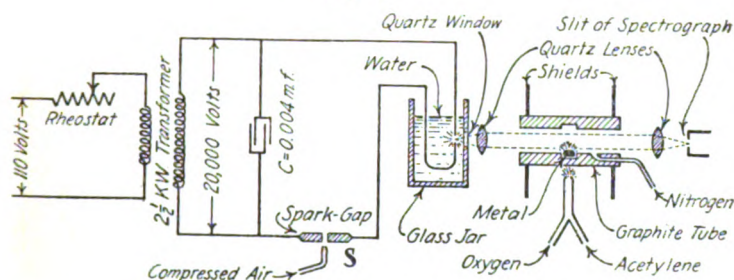
‡‡ Ruark, Mohler, Foote and Chenault, *B. S. Sci. Papers*, 490, p. 468 (1924).

**Table.** They found band and line absorption in Bi and band absorption in Sb vapour.

### Experimental Procedure.

The arrangement of apparatus (fig. 1) was similar to that used by Hulbert\*. A condensed spark under water was used as a source of continuous radiation. A condenser of capacity 0.004 m.f. was charged by means of a 20 kv.  $2\frac{1}{2}$  kw. transformer and discharged through an auxiliary spark gap S, and an under-water spark gap in series. To insure an abrupt discharge compressed air was forced between the terminals of the auxiliary spark gap. Tungsten rods, 3.5 mm. in diameter, and ground to knife edges, served as electrodes for the under-water gap. The radiation from

Fig. 1.



the under-water spark passed directly through the quartz window in the side of the glass jar and then through two quartz lenses, by means of which it was brought to a focus on the slit of the spectrograph. The spectrum thus obtained was continuous except for occasional absorption lines and extended to about 2100 Å.

The graphite tube was about 15 cm. long and had a hole 1.7 cm. in diameter drilled through the centre with a small pocket in the middle to hold the metal under investigation. Through a side tube nitrogen flowed into the graphite tube and thus prevented oxidation of the metal. The central portion of the graphite tube was heated from the outside by means of an oxy-acetylene torch. In this way a sufficient quantity of the metal was vaporized to give satisfactory absorption spectra. Iron shields protected the source of light and the spectrograph from the flame. In the case of some of the metals with lower melting points oxygen and natural gas were substituted for oxygen and acetylene.

\* Hulbert, Phys. Rev. (2) xxiv. p. 129 (1924).

A Féry spectrograph was used throughout the research. In this instrument the collimator and camera lenses are suppressed. The only optical part is the prism, which is traversed by the radiation twice in opposite directions. The curvature of the front and back surfaces of the prism is such that a sharp spectrum is obtained on a photographic film which is bent in the form of a cylindrical surface. The spectrum extends from 2100 Å to 8000 Å and has a length of about 22.4 cm. Eastman Kodak super-speed films were used and were found quite satisfactory. Below 2400 Å the radiation was weak and the films were also less sensitive.

The wave-lengths of the absorption lines were usually found by comparison with the emission spectra. The arc and spark spectra were usually photographed on the same film as the absorption spectra.

### *Experimental Results.*

#### *Zinc.*

The line  $\lambda$  3076, 1S- $2p_{1/2}$ , was strongly absorbed at temperatures around 700° C. The line  $\lambda$  2139, 1S-2P, which had been observed by McLennan and Edwards, failed to appear as an absorption line in any of the eighty exposures. The Cd line  $\lambda$  2288, 1S-2P, appeared on all the zinc photographs. The emission spectrum of the Zn was compared with that of Cd, and it was found that the latter line appeared on both spectrograms. No other Cd line was present in the Zn spectrum. Lead was present as an impurity to the extent of .001 per cent. and the fundamental Pb line  $\lambda$  2833 was strongly absorbed. Fig. 2 (Pl. X.) represents the absorption spectrum of Zn.

#### *Cadmium.*

The results obtained with Cd corroborate the work of Wood and Guthrie on this metal. The two fundamental lines  $\lambda$  3261, 1S- $2p_{1/2}$ , and  $\lambda$  2288, 1S-2P, were strongly absorbed. At high temperatures the latter line widened out into a band nearly 200 Å wide. The line  $\lambda$  3261 appeared at about 600° C. and remained sharp as the temperature was raised. The zinc line 1S- $2p_{1/2}$  appeared on some of the negatives. Fig. 2 (Pl. X.) represents the absorption spectrum of Cd.

#### *Tin.*

The following lines appeared in the Sn absorption spectrum:  $\lambda\lambda$  3009, 2863, 2707, 2483, 2209 and 2171. The

absorption lines in this metal were not nearly so pronounced as in the metals discussed above. The first three listed were observed by Grotrian and the others have been observed as absorption lines by McLennan, Young and McLay.

### Lead.

In addition to the line  $\lambda$  2833, which was found as an impurity in the zinc spectrum, the following lines appeared on the spectrograms :

Wave-length.	Series Notation.
4058 Å	$2p_2-2s$
3684	$2p_3-2x$
3640	$2p_3-2s$
3262	$2p_1-4d_3$
3240	$2p_1-4d_2$
2873	$2p_2-3d_3$
2823	$2p_2-3d_2$
2802	$2p_2-3d_1$
2663	$2p_2-X_2$
2614	$2p_3-3d_2$
2446	$2p_3-3s$
2247	$2p_3-4d_2$
2170	$2p_4-3d_2$

The above notation is taken from Grotrian's paper referred to above. The normal state of the lead atom corresponds to the  $2p_4$  level. The  $2p_1$ ,  $2p_2$ ,  $2p_3$ ,  $2p_4$ , are metastable states. The lines  $\lambda$  2833,  $2p_4-2s$  and 2170,  $2p_4-3d_2$ , which originate from the  $2p_4$  level, are easily absorbed at low temperatures and widen into bands as the temperature is raised. The lines from the metastable states appear at higher temperatures. It is of interest to point out that Zumstein failed to observe the lines  $\lambda$  3260 and  $\lambda$  3240, which originate from the  $2p_1$  level. Grotrian had previously observed these two lines in the lead absorption spectrum.

### Bismuth.

The Bi absorption spectrum is much more complicated than that of any of the preceding metals in that it consists of lines and bands. In the ultra-violet the lines  $\lambda$  3067,  $3d_2-\alpha$ ,  $\lambda$  2276,  $3d_2-\delta$ ,  $\lambda$  2230,  $3d_2-\epsilon$ ,  $\lambda$  2228,  $3d_2-\zeta$ , were strongly absorbed. In the visible, the line  $\lambda$  4254,  $\alpha-\xi$ , was absorbed. Two other absorption lines appeared in the ultra-violet which correspond to the Sb lines  $\lambda$  2293 and



$\lambda 2475$ . However, as no line absorption was detected in Sb vapour it is doubtful if these are true Sb lines. At low temperatures a series of channelled bands appeared, extending from  $2880 \text{ \AA}$  to  $2670 \text{ \AA}$ . These bands merged into one continuous band as the temperature was raised. Another band appeared below  $2200 \text{ \AA}$  at low temperature and extended with rising temperature to about  $2500 \text{ \AA}$ . Another typical band appeared in the visible. This band consisted of two strong absorption lines with finer lines on either side. One of these lines corresponded to the emission line  $\lambda 4254$ , as noted above. A typical spectrogram is reproduced in fig. 2 (Pl. X.). The lines  $\lambda 2230$  and  $\lambda 2228$  do not reproduce as they are within the region of the band. When a larger bead of metal was heated dense clouds of vapour emanated from the cell and the absorption appeared as represented in fig. 2 (Pl. X.) (lower spectrum).

#### Antimony.

No line absorption was detected in Sb vapour. At low temperatures an absorption band appeared below  $2200 \text{ \AA}$  and extended into the visible with increasing temperature. This result is in accord with the photographs published by Dobbie and Fox\*.

#### Discussion.

In the metals of Group II. of the Periodic Table the 1S is the lowest energy level, the 2P being the next lowest. Consequently, atoms of the normal vapour will have their valence electrons in the 1S level and on excitation from some external source will permit them to transfer to the neighbouring 1P level. If the removal is brought about by the absorption of radiant energy, an absorption line of wave number  $\nu = \frac{W_1 - W_2}{h}$  should appear.  $W_1$  is the energy associated with the 1S and  $W_2$  that of the 2P level, and  $h$  is Planck's constant. Similarly, removal of an electron from the 1S to the  $2p_2$  level should give rise to a corresponding absorption line.

The results obtained in Cd vapour are completely in accord with the theory. The 1S—2P line was strongly absorbed at low temperatures. It also appeared in the absorption spectra of several other metals where Cd was present as an impurity of less than .001 per cent. The

\* Dobbie and Fox, Proc. Roy. Soc. A, xcvi. p. 147 (1920).

combination line  $1S-2p_2$  appeared at a higher temperature than the former, but was very prominent.

The results obtained with Zn vapour were not so satisfactory. The line  $1S-2p_2$  was very strongly absorbed but  $1S-2P$  was not detected. As was pointed out above, the Cd line  $1S-2P$  appeared on all the Zn negatives. There is a possibility that this line 2288 Å may be a zinc line as well as a Cd line. It is doubtful, however, that it should be a resonance line for both metals. It is of interest to point out that Tate \* found a resonance potential of 5.65 volts for zinc, whereas the calculated value based on  $\lambda 2139$  is 5.77 volts. If  $\lambda 2288$  were a resonance line of zinc there should be a corresponding resonance potential of 5.4 volts.

The Pb line  $\lambda 2833$  is unquestionably a resonance line for that element. It occurs as an impurity in the absorption spectra of other metallic vapours, and is the most prominent line in the Pb absorption spectrum. It is usually accompanied by  $\lambda 2170$ , which also arises from the  $2p_4$  or lowest level of the Pb atom.

Resonance and ionization potential measurements have been made on metals of Group V. by Foote, Rognley and Mohler †. Their results show that  $\lambda 4722$  and  $\lambda 3067$  are fundamental lines in the Bi spectrum. The latter line has been observed as an absorption line by Grotrian and others. The other line has so far failed to be detected in any absorption experiments. The lines  $\lambda\lambda 2276, 2230$ , and 2228, which were observed by the authors, correspond to electron transfers from the lowest level,  $3d_2$ , to the  $\delta, \epsilon, \zeta$  levels respectively. The line  $\lambda 4254$ , which was observed by the authors, corresponds to a transfer from the  $\alpha$  to the  $\xi$  level.

Band absorption predominates in Sb vapour. In the series arrangement worked out for this metal by Ruark, Mohler, Foote and Chenault, the lines  $\lambda\lambda 2311$  and 3232, arising respectively from the  $3d_2$  and  $3D_1$  levels, are the fundamental lines of the element. However, there is no trace of absorption of either line.

Sept. 12, 1925.

*Note added to MS. on Oct. 2.*—In the September issue of the Phil. Mag. an article appeared on "Absorption of Light by Vapours of Pb, Sn, Bi, Sb and Mg," by Prof. Narayan and Mr. Rao. They found absorption lines in Sb vapour, including the "raie ultime"  $\lambda 2311$ .

\* Tate, Phil. Mag. xxxvi. p. 64 (1918).

† Foote, Rognley and Mohler, Phys. Rev. xiii. p. 59 (1919).

LXVI. *The Wave Form of the Current in an Electrically Maintained Tuning-fork Circuit.* By V. H. L. SEARLE, M.Sc., Assistant Lecturer in Physics, University College of the South-West of England, Exeter\*.

[Plate XI.]

I. *Introduction.*

IN view of the frequent use which is made of the electrically maintained tuning-fork as a standard of frequency it was thought that some interest would attach to an investigation of the form of the current which flows through such a circuit and of the purely electrical factors which exercise decided influence on the current form. Incidentally it was hoped to define, in rather more detail than is possible with frequency measurements, the degree of uniformity of vibration impulse which the various methods possess. The experiments, therefore, had the two-fold aim of comparing different methods of maintenance with one another and the detailed examination of the factors influencing each. This aim has not yet been carried out in its entirety, but the present work gives the results so far obtained and they indicate that further research might disclose interesting facts.

The two circuits which have been studied may be described, for the sake of reference, as the "solid contact" and "mercury break" circuits. By the former is meant the usual method of make and break which employs a platinum-ended screw which, by its intermittent contact with a platinum boss on a small brass piece attached to the fork prong, produces the necessary current variations. By the second, reference is made to the periodic current interruptions due to the withdrawal, by reason of the prong movement, of a platinum wire from the surface of a pool of mercury which acts as one of the current leads. This form of interruption was suggested by Helmholtz and, as will be shown, has a uniformity of action greatly surpassing that of the "solid contact" method.

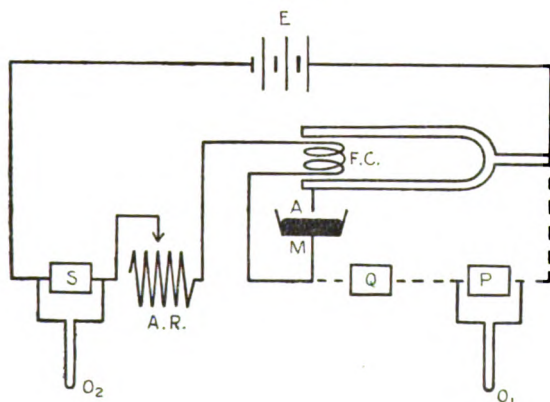
II. *Experimental Results.*

In both investigations the form of circuit shown in fig. 1 was used. E was a 6-volt accumulator which supplied current through an adjustable resistance A.R., a shunt S

\* Communicated by Prof. F. H. Newman, D.Sc.

placed across the oscillator  $O_2$  of a Duddell oscillograph, the make and break contact AM and the coil FC of the fork which had a frequency of 256. The platinum-mercury contact consisted of a wire 12 mm. in length and 0.37 mm. diameter soldered to the fork prong and dipping into a pool of mercury, about 5 mm. deep and 50 mm. across, which was contained in a wooden vessel whose position was adjustable by means of a rising table. Direct current not being available, the mirror of the vibrator  $O_2$  was illuminated by an alternating arc which was found to work much more steadily when, by means of a transformer, the pressure was reduced to 30 volts. The current through the arc was controlled by an iron wire rheostat and, when conditions

Fig. 1.



were favourable for an exposure, this resistance was temporarily cut out and the plate released in the photographic chamber of the oscillograph. In this way a sufficiently brilliant spot of light was obtained to give good density in the negative.

The current form obtained by the "solid contact" method of interruption is shown in Pl. XI. No. I. The arrow indicates the direction of movement of the falling plate, and thus the rise of current, or "make," is distinguished by that ordinate of a crest which is first traced out. It will be noticed that the current builds up rapidly and practically uniformly to its peak value, but that the "break" is rapid at first and then more gradual, causing curvature at the bottom of the wave. Secondly, complete establishment of the maximum current value does not occur at each vibration of the fork

owing to imperfect contact of the platinum points. The same effect causes the small current tremors distinctly noticeable at one of the imperfect contacts, these tremors being due to a rapid vibration of the brass strip carrying the platinum boss. In all the photographs in the plate the periodic changes in the thickness of the lines and the corresponding bands of light across the prints are due to the intensity fluctuations of the arc.

In view of the local irregularities in the "solid contact" wave form attention was directed to the mercury-platinum break, and the current form in the plain circuit of the diagram is shown in No. II. of the Plate. It is immediately noticeable that in this case rather surprising regularity of current variation is obtained, and the result of all experiments with this form of interruption may be here anticipated by the remark that in no instance was a lack of regularity observed. An examination of the wave form shows that, with the mercury break, the "make" is not now linear but proceeds rapidly at first and then more slowly until the peak value is reached. The "break" follows practically the same law as in the mechanical interrupter case. This similarity is probably due to the fact that in both cases an arc is struck and its presence helps to maintain the current—which never drops to a zero value—in the same way.

It was first expected that the mercury break, alone, would be ineffective owing to the agitation of the mercury surface and to the excessive arcing which takes place on "break," but, in practice, it was found that the maintained vibration was exceedingly easy to set up and would continue without attention for long periods—twenty minutes was the longest time actually employed, and in this case the vibration was stopped arbitrarily. The interruption owes its regularity to the forcing, on the mercury surface, of coperiodic stationary ripples so that, at each descent of the platinum point, the conditions of the previous contact are exactly reproduced. It was also noticed that, as the contact point rose from the mercury a ripple crest followed it. The amplitude of the liquid surface immediately below the point was, however, smaller than that of the prong, so the current-strength variation was due to a changing length of mercury arc as well as to a varying degree of ionization.

Since the different characters of the "make" in No. I. and No. II. of the Plate are attributable to the mercury arc, it was anticipated that a condenser across the gap would reproduce the previous form of "make." When the gap was thus shunted it was noticed that the peak value of the

current amplitude decreased and at the same time the current was more nearly completely interrupted. This, of course, would be expected since the condenser practically eliminates the conducting path of the arc. An examination of the corresponding wave form No. III. in the Plate shows that the "make" curve is much more nearly linear while the curvature of the "break" is enhanced. The general property of complete regularity, however, is conserved. It was also found that, contrary to expectations, this circuit showed no superiority over the "plain" circuit in ease of maintenance. Indeed, for easy working, it was advisable to commence the vibration as in the previous case and then to bring in the condenser by means of a plug-key.

The second modification which suggested itself was the introduction into the circuit of an additional source of inductance, and several coils were used varying from a simple air coil of about 50 turns to an iron-cored coil of about 150 turns all on 1 centimetre diameter formers. The only effect noticed was an increased difficulty of maintenance, for no great variation in the current wave form was obtained. This is shown in the companion curves No. IV. *a* and No. IV. *b* of the Plate, in which No. IV. *a* shows the current form when an open cored coil is used, and No. IV. *b* represents the same circuit after the introduction of a soft iron core of  $12\frac{1}{2}$  cm. length and 1 cm. diameter. Comparison of these two curves shows no variation of any moment and, in addition, the shape is the same as No. II. of the Plate. [The change of amplitude is of no significance since this was a result of a change in the ohmic value of the circuit.] It will be shown later by a Fourier analysis of the curve, that the amplitudes of all the harmonics in the current wave form are of small and quickly decreasing values, and thus the effect of additional inductance is confined chiefly to the production of an increased lag angle without material modification of the wave form.

In a final attempt to introduce factors which might be expected to produce deformations in the current form a combination of capacity and inductance was included, the capacity being across the gap and the inductance in series with the rest of the circuit and being additional to that of the fork coil. This modification changed the wave form of the current as can be seen in No. V. *a*, No. V. *b*, and No. V. *c* of the Plate. The inductance was kept constant while the capacity changed progressively. This produced a similarly gradual change in the small deformations which are shown in these photographs. The three typical results

given indicate the change accompanying a variation of capacity from 0.5 to 1.5 m.f.d. It will be noticed that in No. V. *a* there are two local oscillations occurring in the "break" but none in the "make." This indicates that the augmentation of the current which accompanies the rapid reduction in the mercury-gap resistance is sufficient to mask any tendency for the tuned circuit to produce local oscillations, but that on the "break" these oscillations, though small in magnitude, are not completely masked. Comparison between No. V. *a* and No. V. *b* shows an increase in the amplitude of the deformation together with a later occurrence such that the second oscillation now occupies practically the position between "make" and "break." This progression becomes even more manifest in No. V. *c*, where the second oscillation has disappeared and only one kink in the curve is seen, this, however, being of relatively large amplitude. It will be noticed that, while it has been found possible materially to affect the current form, the change is quite definite and the mercury break continues to act with perfect regularity.

### III. Discussion of Results.

If  $E$  is the E.M.F. of the accumulator,  $R_1$  the ohmic resistance of the circuit without the mercury-platinum break,  $L$  the coefficient of self-inductance of the fork coil,  $R$  the ohmic resistance of the gap, and the current  $i$  is connected with the time by the relation  $i = f(t)$ , then the equation connecting these quantities is:

$$L \frac{d}{dt} f(t) + f(t) [R_1 + R] = E, \quad . \quad . \quad . \quad (i.)$$

and a knowledge of  $L$ ,  $f(t)$ ,  $E$ , and  $R_1$  suffices to determine  $R$  which will also be a function of the time.  $E$  and  $R_1$  are easily obtained, while  $f(t)$  and  $L$  were measured as follows.

To determine  $f(t)$  the 12-ordinate scheme, for a Fourier analysis, of C. Runge \* was employed. A travelling microscope measured the distance between two successive positions on the negative of minimum current value, and this length was divided into twelve equal parts by points  $y_0, y_2, y_2 \dots y_{12}$ . The curve ordinates at these points were measured and arranged as shown in Table I.

\* C. Runge, *Zeits. f. Math. und Phys.* xlviii. p. 443 (1903).

TABLE I.

Values of Ordinates	{	2.65	3.04	3.37	3.62	3.35	2.19	1.41
			2.01	1.06	0.45	0.55	0.86	
Sums .....		2.65	5.05	4.43	4.07	3.90	3.05	1.41
Differences .....			1.03	2.31	3.17	2.80	1.33	
		2.65	5.05	4.43	4.07	1.03	2.31	3.17
		1.41	3.05	3.90		1.33	2.80	
Sums .....		4.06	8.10	8.33	4.07	2.36	5.11	3.17
Differences .....		1.24	2.00	0.53		-0.30	-0.49	
		4.06	8.10			2.36	1.24	
		8.33	4.07			3.17	0.53	
Sums .....		12.39	12.17			-0.81	0.71	

Multipliers.	Sine Terms.					Cosine Terms.					
	1st.	5th.	2nd.	4th.	3rd.	1st.	5th.	2nd.	4th.	3rd.	0. 6th.
0.5	1.18					0.27		-4.17	4.05		
0.866		4.43	-0.26	-0.42			1.73				
1.00	3.17				-0.81	1.24		4.06	-4.07	0.71	12.39 12.17
1st Column.	4.35		-0.26		-0.81	1.51		-0.09		0.71	12.39
2nd "	4.43		-0.42			1.73		-0.02			12.17
Sums .....	8.78		-0.68		-0.81	3.24		-0.11		0.71	24.56
Differences.	-0.08		0.16			-0.22		-0.07			0.22
	$A_1 = 1.46$	$A_2 = -0.11$	$A_3 =$			$B_1 = 0.54$	$B_2 = -0.02$	$B_3 =$		$A_0 = 2.05$	
	$A_5 = -0.01$	$A_4 = 0.03$	-0.81			$B_5 = -0.04$	$B_4 = -0.01$	0.12		$B_6 = 0.02$	

We thus have for  $f(t)$  to a first approximation and making a suitable choice of the point  $t=0$ ,

$$i = 2.05 + 1.56 \sin pt.$$

These values are in cms., and to transform them into amperes a calibration of the oscillograph had to be made. This yielded the result :

1 cm. ordinate represented 0.1144 amp.

Thus  $i$ , expressed as amps., becomes :

$$i = 0.235 + 0.177 \sin pt.$$



The ordinary bridge methods of measuring inductance are not easy to apply in the case of a small iron-cored coil. It was therefore decided to use the oscillograph for this purpose. To do this the main lighting current of 60 cycles A.C. was used and a circuit was arranged as shown in fig. 2. The resistances  $R$  and  $r$  provided a means of adjusting the P.D. between  $M$  and  $N$ , and thus of regulating the current value through the fork coil  $FC$ . This current was measured by using the vibrator  $O_2$ . The P.D. across  $FC$  was recorded by the second oscillator  $O_1$  in series with which was a resistance  $X$  large compared with that of  $FC$ . The falling

Fig. 2.

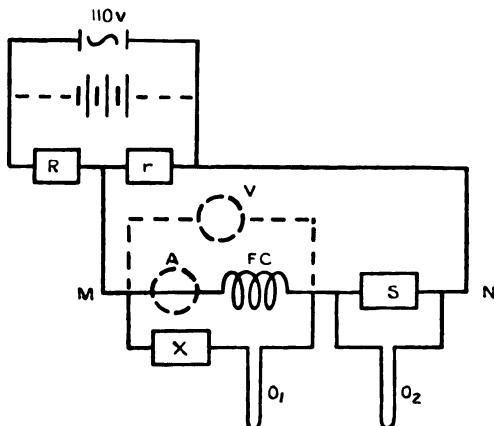


plate thus registered P.D. and current, as is shown in No. VI. of the Plate, the greater amplitude curve being the current form.

To calibrate these curves the circuit was rearranged as shown by the dotted additions in fig. 2. The mains were replaced by a 6-volt accumulator, and a voltmeter  $V$  and an ammeter  $A$  were inserted. This gave two displaced straight lines on the falling plate, and the readings of  $A$  and  $V$  provided calibration values for the 60-cycle curves.

The value of the inductance  $L$  was measured by the use of each of the two formulæ:—

$$I = \frac{E}{\sqrt{R^2 + (2\pi nL)^2}} \quad \dots \dots \dots \text{(ii.)}$$

$$\tan \phi = \frac{2\pi nL}{R}, \quad \dots \dots \dots \text{(iii.)}$$

where  $I$  is the maximum current value,  $E$  the maximum

P.D.,  $R$  the ohmic resistance of FC,  $n$  the frequency of the current, and  $\phi$  the angle of lag.

The values obtained were :

$$\begin{aligned} I &= 0.192 \text{ amp.} & E &= 0.883 \text{ volt.} \\ R &= 4.48 \text{ ohms.} & n &= 60, \quad \phi = 13^\circ.2. \end{aligned}$$

From equation (ii.) we have  $L = 0.0028$  henry.

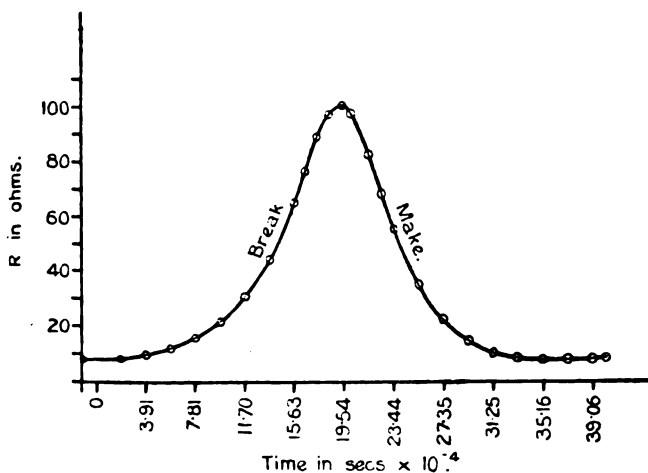
From equation (iii.)  $L = 0.0028$  henry.

If values of  $L$ ,  $f(t)$ ,  $R_1$ , and  $E$  are substituted in equation (i.) it becomes

$$R = \frac{6.36 - 0.767 \cos pt}{0.235 + 0.177 \sin pt} - 8.78. \quad \dots \quad (\text{iv.})$$

This equation indicates how the resistance of the mercury arc varies with time, and when graphed gives the curve

Fig. 3.



shown in fig. 3. Thus the mercury-arc resistance curve is not symmetrical about the maximum ordinate, or in other words the resistance for a given arc length is different on the "make" from on the "break."

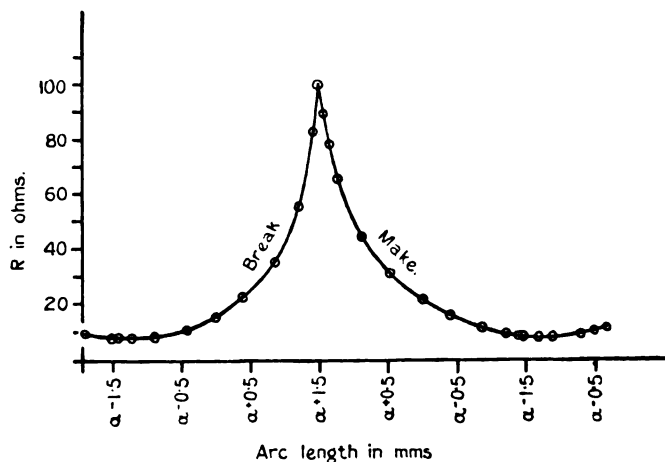
It is an easy matter from this graph to deduce the curve connecting the arc resistance with arc length, since the latter is a known function of the time. It has been stated that the mercury surface oscillates in unison with the fork but with smaller amplitude. The arc length is thus the difference between two expressions of the form  $a + b \sin pt$  and  $c + d \sin pt$ , and is given by  $l = \alpha - \beta \sin pt$ , where  $(\alpha - \beta)$

measures the minimum and  $(\alpha + \beta)$  the maximum separation of the platinum wire from the instantaneous position of the surface immediately beneath it:  $(\alpha - \beta)$  was small but not zero, and  $\beta$  was of the order 1.5 mm. Using this value for  $\beta$ —a change merely alters the scale of the graph—the connexion between arc length  $l$  and resistance  $R$  is obtained by eliminating  $t$  between equation (iv.) and the equation

$$t = \alpha - 1.5 \sin pt.$$

The result of this elimination gives two values of  $R$  for a single value of  $(\alpha - l)$ ; *i. e.*, again it is seen that the “make” resistance for a given arc length differs from the “break” resistance for the same length. The graph connecting  $R$  and  $l$  is shown in fig. 4.

Fig. 4.



It was finally hoped to obtain some check on these results by a combined P.D. and current curve for the circuit examined above. For this the arrangement was as in fig. 1 with the additions shown dotted. The resulting trace is shown in No. VII. of the Plate, and discloses the reciprocal rise of P.D. and fall of current consequent on the changing resistance. This curve, however, could not usefully be calibrated as it was found necessary, in order to obtain a reasonable P.D. amplitude, to have the  $O_1$  vibrator circuit

across the gap of resistance comparable with that of the gap itself. The conditions in this case are, therefore, not strictly comparable with the investigated case.

#### IV. *Summary.*

(i.) Records of the current form in electrically maintained fork circuits were obtained by means of the Duddell oscillograph, and it was found that the "solid contact" means of maintenance acts irregularly. The "mercury-platinum" break—in which a platinum wire fixed to the fork prong dips into, and out from, a mercury surface—however, is very regular and extremely easy to work.

(ii.) Capacity across the spark-gap reduces the current amplitude and affects the shape of the current curve. Inductance does not affect the wave form, but renders maintenance more difficult.

(iii.) By means of a Fourier analysis of the curve and measurement of the constants of the circuit, the variation of mercury arc resistance with time and with arc length has been investigated.

(iv.) The general deductions from (iii.) above are verified by a combined current and potential oscillogram.

#### V. *Description of Plate.*

No. I. Current wave form with "solid contact" method of make and break.

No. II. Current wave form, with "mercury-platinum" method of make and break.

No. III. Same as II., but showing the effect of a condenser across the spark-gap.

No. IV. *a* and No. IV. *b*. Same as II., but showing the effect of an additional source of inductance—IV. *a* without, and IV. *b* with, an iron core.

No. V. *a*, No. V. *b*, and No. V. *c*. Show the effect of a combination of capacity and inductance. The inductance is constant, and the capacity ranges from .5 mfd. to 1.5 mfd.

No. VI. P.D. and current curves for a 60-cycle A.C.

No. VII. P.D. and current curves for the circuit used in No. II.

In conclusion the author would like to express his thanks to Prof. F. H. Newman for suggesting this investigation.

LXVII. *The Application of the Rigorous Quotient Theorem.*  
 By ALEXANDER BROWN, *Professor of Applied Mathematics,*  
*University of Cape Town* \*.

§ 1. **I**N Tensor Theory considerable use is made of the 'Rigorous Quotient Theorem,' viz.: "A quantity which on inner multiplication by *any* covariant (or *any* contravariant) tensor always gives a tensor is itself a tensor." Attention is here called to the need that the multiplying tensor be completely arbitrary. If the tensor used in forming the product be in any way restricted the theorem cannot be used; but in certain cases other inferences may be made. This is illustrated below by reference to cases where apparently incorrect application has been made of the theorem, and to conclusions that can be drawn in particular cases where the tensor used is not perfectly arbitrary.

§ 2. In finding the covariant derivative of a tensor one of the conditions we have to satisfy is that the quantity sought is a three-rank tensor. Eddington ('Math. Theory of Relativity,' § 30) uses the Rigorous Quotient Theorem for this purpose thus: differentiate the invariant

$$A_{\mu\nu} \frac{dx_\mu}{ds} \cdot \frac{dx_\nu}{ds}$$

along a geodesic and substitute for  $\frac{d^2x_\mu}{ds^2}$  from the geodesic equation; we then find the invariant expression

$$\begin{aligned} \frac{\partial A_{\mu\nu}}{\partial x_\sigma} \cdot \frac{dx_\sigma}{ds} \cdot \frac{dx_\mu}{ds} \cdot \frac{dx_\nu}{ds} - A_{\mu\nu} \{ \beta \gamma, \mu \} \frac{dx_\beta}{ds} \cdot \frac{dx_\gamma}{ds} \cdot \frac{dx_\nu}{ds} \\ - A_{\mu\nu} \{ \delta \epsilon, \nu \} \frac{dx_\delta}{ds} \cdot \frac{dx_\epsilon}{ds} \cdot \frac{dx_\nu}{ds}. \quad (1.1) \end{aligned}$$

In this expression all the suffixes are dummy suffixes and can be changed and interchanged in various ways. Leave the first term in (1.1) as it is; in the second change  $\mu$  into  $\alpha$ ,  $\beta$  into  $\mu$ , and  $\gamma$  into  $\sigma$ ; and in the third change  $\nu$  into  $\alpha$ ,  $\delta$  into  $\mu$ , and  $\epsilon$  into  $\sigma$ ; (1.1) now becomes

$$\left( \frac{\partial A_{\mu\nu}}{\partial x_\sigma} - \{ \mu \sigma, \alpha \} A_{\alpha\nu} - \{ \nu \sigma, \alpha \} A_{\mu\alpha} \right) \frac{dx_\mu}{ds} \cdot \frac{dx_\nu}{ds} \cdot \frac{dx_\sigma}{ds}, \quad (1.2)$$

\* Communicated by Prof. A. S. Eddington.

and it is inferred that the coefficient

$$A_{\mu\nu\sigma} \equiv \frac{\partial A_{\mu\nu}}{\partial x_\sigma} - \{\mu\sigma, \alpha\} A_{\alpha\nu} - \{\nu\sigma, \alpha\} A_{\mu\alpha}$$

is a 3-rank covariant tensor by application of the Rigorous Quotient Theorem.

It appears, however, that the reasoning here is not legitimate. The result obtained is correct, as can be verified by direct transformation; but this correct result is only one out of several that can be obtained by identical reasoning, and it appears an accident that the true result has been chosen instead of one of the false ones.

To get (1.1) into a form suitable for the application of the Rigorous Quotient Theorem we must transform the sets  $\beta\gamma\nu$  and  $\delta\epsilon\mu$  each into  $\mu\nu\sigma$ . For the former of these, six methods of substitution are possible which, with the corresponding factors, are tabulated below:

$\beta$ .	$\gamma$ .	$\nu$ .	Factor.	} \quad . \quad . \quad . \quad (1.3)
$\sigma$	$\mu$	$\nu$	$A_{\alpha\nu}\{\sigma\mu, \alpha\}$	
$\sigma$	$\nu$	$\mu$	$A_{\alpha\mu}\{\sigma\nu, \alpha\}$	
$\mu$	$\sigma$	$\nu$	$A_{\alpha\nu}\{\mu\sigma, \alpha\}$	
$\mu$	$\nu$	$\sigma$	$A_{\alpha\sigma}\{\mu\nu, \alpha\}$	
$\nu$	$\mu$	$\sigma$	$A_{\alpha\sigma}\{\nu\mu, \alpha\}$	
$\nu$	$\sigma$	$\mu$	$A_{\alpha\mu}\{\nu\sigma, \alpha\}$	

We get the same set precisely from the third term of (1.1). Hence

$$\left( \frac{\partial A_{\mu\nu}}{\partial x_\sigma} - J - K \right) \frac{dx_\mu}{ds} \cdot \frac{dx_\nu}{ds} \cdot \frac{dx_\sigma}{ds}$$

is an invariant where J and K are any of the six factors in (1.3). If the Rigorous Quotient Theorem were applicable,

we should conclude that  $\frac{\partial A_{\mu\nu}}{\partial x_\sigma} - J - K$  was a 3-rank tensor,

which, as a matter of fact, is not the case for some groupings of the J's and K's.

§ 3. The reason why the Theorem is not applicable here

is that one of its conditions is not fulfilled;  $\frac{dx_\mu}{ds} \cdot \frac{dx_\nu}{ds} \cdot \frac{dx_\sigma}{ds}$

is not an arbitrary 3-rank tensor; it is a special tensor—the outer product of three vectors, and it is familiar that an arbitrary 3-rank tensor cannot be expressed as the outer product of three vectors. From another point of view it

has only 20 distinct elements instead of the 64 belonging to the arbitrary tensor of this rank.

§ 4. To find what inferences can be drawn from the invariance of quantities like (1.2), it is necessary to retrace the steps in the proof of the Rigorous Quotient Theorem.

As a simple case suppose we are given that

$$A_{\mu\nu} \cdot dx_\mu \cdot dx_\nu \text{ is invariant,} \quad . \quad . \quad . \quad (2.1)$$

$$\text{i. e.} \quad A'_{\alpha\beta} \cdot dx'_\alpha \cdot dx'_\beta = A_{\mu\nu} \cdot dx_\mu \cdot dx_\nu$$

$$= A_{\mu\nu} \cdot \frac{\partial x_\mu}{\partial x'_\alpha} \cdot \frac{\partial x_\nu}{\partial x'_\beta} \cdot dx'_\alpha \cdot dx'_\beta.$$

$$\therefore \quad \left( A'_{\alpha\beta} - \frac{\partial x_\mu}{\partial x'_\alpha} \cdot \frac{\partial x_\nu}{\partial x'_\beta} \cdot A_{\mu\nu} \right) dx'_\alpha \cdot dx'_\beta = 0. \quad . \quad (2.2)$$

In this, the elements  $dx'_\alpha \cdot dx'_\beta$  are not all independent; thus  $\alpha=1, \beta=2$  and  $\alpha=2, \beta=1$  give the same element; so that we cannot say that the coefficient belonging to  $\alpha=2, \beta=1$  vanishes but only that the sum of the coefficients belonging to  $\alpha=2, \beta=1$  and  $\alpha=1, \beta=2$  vanishes.

Hence from (2.2) we deduce, if  $\alpha$  and  $\beta$  are the same,

$$A'_{\gamma\gamma} = \frac{\partial x_\mu}{\partial x'_\gamma} \cdot \frac{\partial x_\nu}{\partial x'_\gamma} \cdot A_{\mu\nu}, \quad . \quad . \quad . \quad (2.3)$$

while if  $\alpha$  and  $\beta$  are different,

$$A'_{\alpha\beta} - \frac{\partial x_\mu}{\partial x'_\alpha} \cdot \frac{\partial x_\nu}{\partial x'_\beta} \cdot A_{\mu\nu} + A'_{\beta\alpha} - \frac{\partial x_\mu}{\partial x'_\beta} \cdot \frac{\partial x_\nu}{\partial x'_\alpha} \cdot A_{\mu\nu} = 0. \quad (2.4)$$

The last term in (2.4) can be written

$$- \frac{\partial x_\mu}{\partial x'_\beta} \cdot \frac{\partial x_\nu}{\partial x'_\alpha} \cdot A_{\nu\mu},$$

so that (2.4) can be written

$$A'_{\alpha\beta} + A'_{\beta\alpha} = \frac{\partial x_\mu}{\partial x'_\alpha} \cdot \frac{\partial x_\nu}{\partial x'_\beta} (A_{\mu\nu} + A_{\nu\mu}). \quad . \quad . \quad (2.5)$$

If now we write

$$\frac{1}{2}(A_{\mu\nu} + A_{\nu\mu}) = B_{\mu\nu} = B_{\nu\mu}$$

$$\text{and} \quad \frac{1}{2}(A'_{\alpha\beta} + A'_{\beta\alpha}) = B'_{\alpha\beta} = B'_{\beta\alpha},$$

$$\text{then} \quad B'_{\alpha\beta} = \frac{\partial x_\mu}{\partial x'_\alpha} \cdot \frac{\partial x_\nu}{\partial x'_\beta} \cdot B_{\mu\nu}, \quad . \quad . \quad . \quad (2.6)$$

so that  $B_{\mu\nu}$  is a tensor.

If the  $A$ 's are symmetrical so that  $A_{\alpha\beta} = A_{\beta\alpha}$ , then  $B_{\alpha\beta} = A_{\alpha\beta}$ , and  $A_{\mu\nu}$  is a tensor.

For example, the invariance of  $g_{\mu\nu} \cdot dx_\mu \cdot dx_\nu$  combined with the symmetry of  $g_{\mu\nu}$  establishes the fact that  $g_{\mu\nu}$  is a tensor.

On the other hand, we may write

$$ds^2 = (g_{\mu\nu} + F_{\mu\nu}) dx_\mu \cdot dx_\nu,$$

where  $F_{\mu\nu}$  is any antisymmetrical function of  $\mu$  and  $\nu$ , without altering the value of  $ds^2$ ; and it does not follow that  $g_{\mu\nu} + F_{\mu\nu}$  is a tensor.

In Eddington, § 29, it is shown that

$$\frac{dx}{ds} \cdot \frac{dx_\nu}{ds} \left( \frac{\partial A_\mu}{\partial x_\nu} - \{\mu\nu, \alpha\} A_\alpha \right) \text{ is invariant ;}$$

we cannot infer that the quantity in brackets is a tensor but only that

$$\frac{1}{2} \left( \frac{\partial A_\mu}{\partial x_\nu} + \frac{\partial A_\nu}{\partial x_\mu} \right) - \{\mu\nu, \alpha\} A_\alpha \text{ is a tensor.}$$

§ 5. Similar results hold for higher tensors.

Thus, if in a 3-dimensional system the quantity

$$A_{\mu\nu\sigma} \cdot dx_\mu \cdot dx_\nu \cdot dx_\sigma$$

is invariant, we cannot infer that  $A_{\mu\nu\sigma}$  is a tensor.

On the other hand,  $B_{\mu\nu\sigma}$  is a tensor where

$$B_{aaa} = A_{aaa}$$

$$B_{aab} = B_{aba} = B_{baa} = \frac{1}{3} (A_{aab} + A_{aba} + A_{baa})$$

$$B_{abc} = B_{acb} = B_{bac} = B_{bca} = B_{cab} = B_{cba}$$

$$= \frac{1}{6} (A_{abc} + A_{acb} + A_{bac} + A_{bca} + A_{cab} + A_{cba}),$$

the twenty-seven elements of the tensor being represented by only ten distinct quantities.

[This limitation of the quotient law is mentioned in the *second* edition of my 'Mathematical Theory of Relativity' (Note 2, p. 242), which Prof. Brown will not have seen; but the point is of much importance, and I welcome his discussion of it. For the sake of clearness it should be pointed out that in my enunciation of the rigorous quotient theorem the multiplier is a *vector*, not a general tensor as in Brown's enunciation; and that his remarks refer in most cases to what I have called the argument from covariant dimensions which is not claimed to be rigorous. That does not in any way diminish their value and instructiveness. In general I did not trouble about rigour in the deduction of the various tensors, since the main point was the method of discovery of the expressions; once found, their tensor character could be tested in other ways, but any proof that  $g_{\mu\nu}$  is a tensor professed to be rigorous, and in this case I fell into the trap similar to the one which Prof. Brown here exposes.—A. S. EDDINGTON.]



# LXVIII. *A Method for Exciting Spectra of Certain Metals.*

By JOHN K. ROBERTSON, *Associate Professor of Physics, Queen's University, Kingston, Canada*.\*

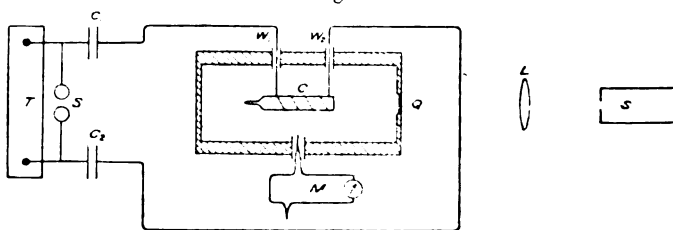
[Plate XII.]

## *Introduction.*

A YEAR or more ago, in order to obtain information which might prove of value in analysing the spark spectrum of tin, an attempt was made to excite the vapour of that element by the use of the electrodeless discharge. Because of residual gas which developed at the high temperature at which it was necessary to work, the attempt was only partially successful. A control spectrum of the discharge carried by the residual gas in the tube at room temperature, however, revealed an interesting result. *Characteristic tin lines were present in this spectrum almost to the same extent as in those obtained with the tube at a temperature in the neighbourhood of  $1000^{\circ}\text{C}$ .* As the vapour pressure of tin under conditions of the control spectrum could not have exceeded  $10^{-20}$  mm., the origin of the metallic lines in this case was somewhat puzzling, and it seemed worth while to see if the same effect could be obtained with other metals. This was done with zinc, cadmium, silver, and gold with results which, together with a discussion of the possible cause of the appearance of the lines, are reported in the present paper.

## *Experimental.*

Fig. 1.



To obtain an electrodeless discharge in tin vapour, it was obvious at the outset that temperatures at least as high as  $1000^{\circ}\text{C}$ . would be necessary. For that purpose a cylindrically shaped oven was constructed with a quartz window  $Q$  at the centre of one end, and with inlets for the insertion of one junction of a thermocouple  $M$  and for the high-frequency leads

\* Communicated by the Author.

$W_1$  and  $W_2$ . These leads were the ends of a cylindrical coil C of heavy nickel wire, consisting of 12 turns tightly wrapped around an alundum tube supported along the horizontal central axis of the oven. To obtain high-frequency currents, leyden jars  $C_1$  and  $C_2$  were charged by means of a small interrupterless X-ray transformer T, while the intensity of discharge in the oscillatory circuit containing the condensers and the coil C was controlled by means of the spark-gap S. Frequencies of the order of  $10^8$  per second were used. A highly exhausted cylindrical quartz tube, 3.2 cm. in diameter, 15 cm. long, containing pure tin, was placed within the alundum tube and exciting coil. As the quartz tube had previously been subjected to a careful preliminary outgassing and heating, it was hoped that a pure tin discharge would be obtained when the sealed-off tube was heated to  $1000^\circ\text{C}$ . To examine the spectrum of any such discharge light from the quartz tube was focussed, by means of the quartz lens L, on the slit of a small Hilger spectrograph S.

With the first tube discharges were obtained and spectrograms taken at temperatures ranging from  $700^\circ\text{C}$ . to  $1000^\circ\text{C}$ ., in some cases with different degrees of excitation. It was evident, however, that at least part of the discharge was carried by residual gas. This may readily be seen by an examination of a typical spectrogram shown in Plate XII. (fig. 2 a), in which, in addition to the prominent arc and a few spark lines of tin, some due to gas and to other impurities are present. Attention may also be directed to the fact that, in spite of the use of liquid air and phosphorus pentoxide, the characteristic water-vapour band with head at 3064 is strongly developed.

The tube was now re-opened, attached to the evacuating system, washed out, when hot, with hydrogen to reduce possible oxides, and finally subjected to further heating and outgassing in the hope of removing all traces of residual gas and water vapour. On sealing off from the pumps the tube was once more placed in the oven and photographs taken of the spectrum of the discharge obtained at  $900^\circ\text{C}$ . or higher. In Plate XII. (fig. 2 b) the result is shown. Residual gas and water vapour are still present, while, in spite of the use of liquid air, a few mercury lines have made their appearance. It is significant that tin lines are considerably less prominent in this spectrum than in fig. 2 a, where mercury lines are absent.

In view of the failure to remove completely residual gas and water vapour, it was next decided to see if, with a new tube, a pure tin discharge could not be obtained with the tube

attached to the evacuating system while at the same time it was heated in the oven to  $1000^{\circ}\text{C}$ . Under these conditions absolutely no discharge was obtained, although a deposit of tin gradually became visible on the walls of a portion of the connecting tube outside the oven. At this temperature a vapour pressure sufficiently high to permit of a discharge could not be obtained—at any rate, maintained—inside the tube. This tube was now subjected to a very drastic heating and outgassing, and once more an attempt was made to obtain a pure tin discharge when the sealed tube was used.

This time somewhat better success was attained, as initially a continuous discharge was not obtained until a temperature in the neighbourhood of  $900^{\circ}\text{C}$ . was reached, an indication that residual gas was not present to any marked degree. The discharge then obtained was characterized by a general glow, of slightly bluish cast which deepened as the temperature rose slightly. Its spectrum revealed a continuous region extending from  $2000\text{ \AA.U.}$  almost to the visible region, together with tin arc lines superimposed and certain impurities. At  $1000^{\circ}\text{C}$ . the characteristic white *ring* discharge developed, as will be evident from the increased intensity at the outer edges of the spectrogram in Plate XII. (fig. 3 a). It will be noticed that the water-vapour band is again present. Unfortunately, while the exposure for this plate was in progress, a short-circuiting of one of the heating coils in the oven caused a rise in temperature higher than any which had hitherto developed and the discharge disappeared. This was doubtless due to the development of a gas pressure above that at which an electrodeless discharge could be obtained, for on cooling the tube, a bright discharge could be obtained at room temperature without difficulty. A control spectrum taken with the tube "cold," and shown in Plate XII. (fig. 3 c), revealed an interesting result. As is clearly shown in the reproduction, *almost all the strong lines below 3000 are due to tin, and, with few exceptions, characteristic tin lines are present in this spectrum to the same extent as in fig. 3 a, that taken at  $1000^{\circ}\text{C}$ .* This result was corroborated by examination of a spectrogram taken, purely for purposes of alignment, when the attempt was made to obtain a tin discharge with the tube attached to the pumping system. In this case, air at a pressure of the order of  $1/10\text{ mm.}$  had been left in the apparatus to carry the discharge, while the tube contained metallic tin. In Plate XII. (fig. 3 b) the spectrum obtained under such conditions has been placed alongside those corresponding to the "cold" and the  $1000^{\circ}\text{C}$ . discharges, and again it will be noticed that in fig. 3 b tin

lines have come out much as in the other two. As an ordinary dry plate was used to obtain this spectrogram, and Schumann plates for 3a and 3c, the effect is not so striking.

At this stage, therefore, the writer was interested in two questions: (1) Where did the water vapour come from? (2) What was the origin of the tin lines occurring at temperatures corresponding to which the vapour pressure is extremely low?

A visit to the Research Laboratory of the General Electric Company, Schenectady, N. Y., supplied the answer to the first question. The experience of workers in that laboratory has shown that water vapour is given off from hot quartz and that it is a very difficult matter to get rid of it. In spite of careful outgassing, therefore, in the experimental conditions described above, the presence of the water-vapour band is not surprising.

To provide additional information which would probably help to answer the second question, it was obviously desirable to see if the same effect could be obtained with other metals. This was done with cadmium, zinc, silver, gold, and again with tin to verify earlier work. In all subsequent work the quartz tube was attached to the evacuating system and sufficient gas was left in the apparatus to carry the discharge. As hydrogen lines had been prominent in the early work, for the most part this gas, at a pressure of 1/10 mm. or less, was used and spectrograms were made with a U-tube immersed in liquid air to keep mercury vapour out of the quartz tube.

### *Cadmium.*

In the case of cadmium, Plate XII. (fig. 4) shows the

TABLE II.

Wave-length.	Series Notation.	
2144	$1\sigma - 1\pi_1$	Cd +
2265	$1\sigma - 1\pi_2$	Cd +
2288	$1S - 1P$	Cd
3261	$1S - 1p_2$	Cd

result obtained with the quartz spectrograph. Only the few lines given in Table II. came out with marked intensity.

Other lines were entirely absent, with the exception of one or two whose intensity was many times less than that of those given in the table. Another spectrogram taken with a glass prism spectrograph in the visible region showed the triplet 5086, 4800, 4678 ( $1p-1s$ ) strongly developed, and a line which is possibly 4413 ( $1p_2-2S$ ).

It will be evident, therefore, that the only lines which appear with considerable intensity are ultimate and penultimate lines of the neutral atom, together with ultimate lines of the ionized element\*. The significance of this will be discussed later.

### *Zinc.*

In the case of zinc similar results were obtained. The few lines which stood out prominently in the ultra-violet, as shown in Plate XII. (fig. 5) and in Table III., are again ultimate or penultimate lines of the neutral, together with two ultimate of the ionized atom. As the quartz tube used for this metal had been previously used for cadmium, in spite of careful cleaning a few cadmium lines are present.

TABLE III.

Wave-length.	Series Notation.	
2025	$1\sigma - 1\pi_1$	Zn+
2062	$1\sigma - 1\pi_2$	Zn+
2133	$1S - 1P$	Zn
3302	$1p_1 - 2d$	Zn
3345	$1p_2 - 2d$	Zn

In repeating observations with tin under similar conditions, it was shown not only that the characteristic lines came out to much the same extent as in earlier work, but also that it was not necessary to have a deposit of metal on the tube. There was little difference in two spectrograms taken, one before fresh pieces of tin had been subjected to any heating, the other after an oxygen-gas flame had been played on the tube until a visible deposit had formed on the walls of the tube.

\* For explanation of these terms see Russell, *Astrophys. J.* iv. p. 223 (1925).

*Mercury.*

Attention has already been directed to the fact that in Plate XII. (fig. 2 *b*) a few mercury lines are evident. An examination of these shows the presence, with considerable intensity, of two lines usually assigned to the ionized atom, together with ultimate and penultimate neutral lines, the strongest of which below 3000 are shown in Table IV.

TABLE IV.

Wave-length.	Series Notation.		Intensity.
2224.8	?	Hg +	Strong.
2536.5	1s - 1p <sub>2</sub>	Hg	"
2847.8	?	Hg +	"
2967.3	1p <sub>2</sub> - 2d	Hg	"
2652 ±	1p <sub>2</sub> - 3d	Hg	Weak.
2893.6	1p <sub>2</sub> - 2s	Hg	"

*Silver and Gold.*

With these metals negative results were obtained, although it should be stated that in the case of silver, the lines to be expected, 3383 and 3280, are in the region of small dispersion where it is difficult to identify lines with certainty.

To sum up, then, it has been shown that, by allowing a gas to carry an electrodeless discharge in a tube in which a metal has been placed, spectral lines characteristic of the metal are brought out in the case of tin, cadmium, and zinc. Moreover, the zinc and cadmium lines, which are few in number, are fundamental, both as regards the neutral and the ionized atom.

*Discussion.*

In seeking for the origin of these metallic lines, two possible causes suggest themselves: (1) The effect is simply one of vaporization, as a result of which sufficient atoms are present in the discharge region to give rise to lines of marked intensity. (2) The atoms of the metal are present as a result of a reaction, chemical or otherwise, between excited gas atoms and the metal or an oxide of the metal. We shall first of all examine the evidence for and against the vaporization theory.

Although the discharge begins at room temperature, there is considerable energy absorbed and after an exposure of ten or fifteen minutes the exciting coil as well as the quartz tube are decidedly warm. A piece of metal or thin metallic layer, therefore, would rise in temperature considerably. To obtain some idea of the magnitude of such a rise, a Brown thermocouple was placed within the exciting coil, (a) within a thin copper shield, (b) without the copper shield. In the second case, after 15 minutes there was a rise in temperature to  $100^{\circ}\text{C.}$  without any sign of a maximum, while, with the shield, after 10 minutes a temperature of  $125^{\circ}$ , approaching a maximum, had been recorded. There seems no doubt, therefore, that the metal would become hot. On the other hand, pieces of tin (melting-point =  $232^{\circ}\text{C.}$ ) did not melt, so that we may reasonably assume  $200^{\circ}\text{C.}$  as an upper limit to the possible temperature attained during the time of exposure. In some cases this was less than 10 minutes.

TABLE V.

Metal.	$100^{\circ}\text{C.}$	$200^{\circ}\text{C.}$
Od .....	$4 \times 10^{-5}\text{ mm.}$	$2 \times 10^{-3}\text{ mm.}$
Zn .....	$3 \times 10^{-6}\text{ ,,}$	$9 \times 10^{-4}\text{ ,,}$
Sn .....	$4 \times 10^{-24}\text{ ,,}$	$9 \times 10^{-18}\text{ ,,}$
Au .....	$5.5 \times 10^{-26}\text{ ,,}$	$5 \times 10^{-20}\text{ ,,}$
Ag .....	$4 \times 10^{-18}\text{ ,,}$	$1 \times 10^{-13}\text{ ,,}$

In Table V. approximate vapour pressures of cadmium, zinc, tin, gold, and silver have been given at temperatures of  $100^{\circ}\text{C.}$  and  $200^{\circ}\text{C.}$  A glance at this table will show that in the case of cadmium and zinc, undoubtedly ordinary vaporization may be responsible for the effect observed. In this connexion it should be stated that a visible cadmium deposit was formed in the tube, but none with zinc. In the case of tin, however, we can reasonably conclude that the vapour pressure could not possibly exceed  $10^{-20}\text{ mm.}$  Can we detect spectral lines with such a low pressure? That is a question which experiment alone can answer, and the writer has under way an investigation designed to throw light on the matter. In the meantime it seems extremely unlikely that lines as strong as those shown in Plate XII. (fig. 3 c), for

example, could come out with a vapour density as low as that corresponding to such a pressure. It is doubtful, therefore, if ordinary vaporization due to rise in temperature can be the cause in the case of tin, and it does not necessarily follow that it must be so even for cadmium and zinc. Confirmation of the probable correctness of this conclusion is found in the work of Goldstein\* on the appearance of metallic lines in the discharge of a vacuum tube containing nitrogen. Not only were lines characteristic of the metallic cathode present, but they appeared with increased intensity when the vacuum-tube was immersed in liquid air.

The spectroscopic information obtained by the writer is not without its significance. In the case of zinc, cadmium, and mercury it has already been emphasized that ultimate lines of the ionized atom were present, while higher members of the ordinary arc series were either absent or of feeble intensity. This result is somewhat surprising. Why should ultimate lines of the ionized atom appear with marked intensity, while higher members of arc series, which require less excitation, are absent altogether? If metallic atoms were in the discharge region as a result of ordinary vaporization, it is difficult to see why this should be the case. Undoubtedly with hydrogen carrying the discharge, there would be many electrons present with sufficient velocity to ionize these metallic atoms, and the resulting ions could easily be excited to radiation. At the same time, however, higher members of neutral series should come out. This is all the more to be expected when the pressure of the vapour is a small fraction of the total, for, in that case, the "expectation of life" of the neutral atom is increased.

In this connexion reference may be made to the somewhat related work of Merton and Pilley† on nitrogen and Paschen‡ on aluminium. The former investigators showed that when a feebly condensed discharge took place in helium (at 30 mm. pressure) which contained an "extremely small amount" of nitrogen, a true arc spectrum of this gas was obtained "completely isolated from the spark." Conditions, however, were by no means identical with those we are discussing, for comparatively few electrons sufficient to ionize nitrogen atoms were present.

Paschen, using a discharge in a vacuum-tube, with a cylindrical cathode of aluminium containing pure helium,

\* Goldstein, *Phys. Zeitschr.* vi. p. 14 (1905).

† Merton and Pilley, *Proc. Roy. Soc. A*, cvii. p. 411 (1925).

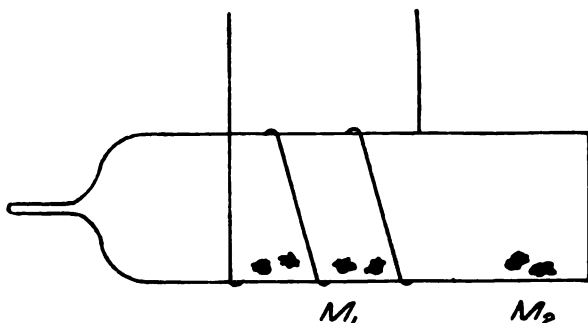
‡ Paschen, *Ann. d. Phys.* lxxi. p. 142 (1923).



found that lines of neutral and singly ionized atoms (Al I and II) came out, whereas in the ordinary spark lines of Al I, II, and III were present. Moreover, higher members of Al II were present in the case where a trace of the vapour was present in the discharge than in the Al II of the ordinary spark. It seems remarkable, therefore, that in the case of the electrodeless excitation higher members of arc series should be absent and ultimate ionized lines present.

Something may be said in favour of the other possible explanation, that metallic ions find themselves in the discharge region as a result of some kind of reaction between active gas atoms or gas ions and the metal or an oxide of the metal. In the first place, pieces of metal lying in the high-frequency field are undoubtedly in a favourable state for such a reaction. Evidence of this is found in the work of Bloch and Bloch\* on sodium chloride. These investigators have found that when a high vacuum has been attained in a tube containing this salt, an electrodeless discharge takes place with

Fig. 6.



chlorine lines very prominent. Moreover, once the excitation is removed, it is necessary to re-admit air in the apparatus and to re-exhaust before the "chlorine" discharge can again be obtained. In the present investigation it was observed that pieces of zinc placed directly within the exciting field, as at  $M_1$ , fig. 6, had completely lost the whitish-grey coating usually to be found on that metal, whereas other pieces outside the field, as at  $M_2$ , remained in the original condition. It looks, therefore, as if a kind of cleaning up process was at work, and it is not improbable that a reduction of an oxide took place, zinc ions being liberated in the process.

\* Bloch and Bloch, *Compt. Rend.* clxxx. p. 1740 (1925).

As in the case of tin, air was as effective as hydrogen in bringing out metallic lines, the oxide theory is not altogether satisfactory. It may be that the metal is put in a favourable state so that metal ions are pulled off, as it were, as a result of bombardment by the gaseous ions carrying the discharge. Some work of Langmuir shows that, under certain conditions, metallic coatings on walls may be removed by such means. Regarding this point additional information might be obtained by the use of an inactive residual gas such as helium, and, in the near future, the writer hopes to make such a test.

If metallic *ions*, not neutral atoms, find themselves in the discharge region because of some such reaction, then a possible explanation of the appearance of ultimate ionized lines, and non-appearance of higher members of neutral series, may be suggested. Some of these ions would be excited to radiation, possibly as a result of collisions of the second kind, while many neutral atoms would be formed by re-combination. Such atoms would subsequently be excited, but because of the excess of low-voltage electrons, which it is not improbable to assume exists in the alternating electrodeless field, ultimate and penultimate lines would greatly exceed in intensity higher members of neutral series. The same explanation might reasonably be applied to mercury, for the presence of this vapour (in fig. 2 *b*) may have been the result of the formation of an oxide of that element when the hot tube was being washed out with hydrogen.

Whatever the explanation of the effect, the result should be of value in spectroscopic analysis. Any method which throws into relief fundamental spectral lines is valuable, and the writer hopes to put this one to use, not only in work on the spectrum of tin but in the case of other metals.

The writer has pleasure in acknowledging his indebtedness to the Research Council of Canada for a grant which enabled him to purchase quartz apparatus; to Mr. J. T. Thwaites, B.Sc., for assistance in constructing the electric oven, and to the Electrical Alloy Company of Morristown, N.J., for the gift of a coil of heavy nickel wire.

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Queen's University,  
Kingston, Canada,  
November, 1925.

LXIX. *The Evacuation of Carbon Dioxide and Water.* By N. R. CAMPBELL. (Communication from the Staff of the Research Laboratories of the General Electric Co., Wembley)\*.

#### SUMMARY.

WHEN a cooled trap is used for removing mercury vapour, there is a danger that substances may condense in the trap and establish in the vessel to be evacuated a pressure, large enough to be appreciable, yet small enough to prevent the rapid removal of the substance by the pump. If the trap is cooled in liquid oxygen boiling at atmospheric pressure, carbon dioxide condenses in this manner; if solid  $\text{CO}_2$  is used, water condenses. Accordingly if these substances are present and a pressure is to be obtained as low as that possible in their absence, the trap must be maintained at some other temperature. It can easily be maintained (1) at  $78^\circ\text{K}$ . by boiling the oxygen under reduced pressure or (2) between  $108^\circ$  and  $150^\circ\text{K}$ . by means of solid mercury cooled by liquid oxygen. At either of these temperatures, pressures less than  $10^{-7}$  mm. can be obtained quickly, even if water and carbon dioxide are present. The vapour pressure of  $\text{CO}_2$  at  $90^\circ\cdot2\text{K}$ . is a convenient standard for calibrating ionization gauges.

WHEN a cooled trap to absorb mercury vapour is placed in a pumping circuit, the evacuation involves two distinct processes. Gases such as oxygen are removed by pumping, mercury vapour by condensation at a temperature at which its vapour pressure is inappreciable. It does not seem always to be realized that this combination of two processes may lead to the failure of both. If there is present in the system a substance of which the vapour pressure at the temperature of the trap is of the order of  $10^{-5}$  mm., its vapour pressure will be appreciable and greater than that easily attained by the pump, and yet it will be so low that the substance will be pumped away extremely slowly. It will be "condensed" in the trap, but it will establish on the far side of it a constant pressure which will be independent of the action of the pump and will not fall until the whole of the substance has been removed. If the pressure is  $10^{-5}$  mm. and the effective volumetric speed of the pump 1 litre per second, the removal of gas occupying 1 c.c. at N.T.P. will require 21 hours.

The temperatures at which such a trap are most often

\* Communicated by the Director.

maintained are  $194^{\circ}\cdot 9$  K. (solid  $\text{CO}_2$ ) and  $90^{\circ}\cdot 2$  K. (liquid oxygen). The "condensable" gases (other than mercury) most likely to be present in a pumping system are water and carbon dioxide. It is unfortunate that at the higher temperature water, and at the lower carbon dioxide, has a vapour pressure within or near the dangerous range. The vapour pressure of water (ice) at temperatures above  $200^{\circ}$  K. has been measured by Scheel and Hause\*; we have discovered no measurements at lower temperatures, but by extrapolating their formula

$$\log_{10} p(\text{mm.}) = 11\cdot 50406 - 0\cdot 4 \log_{10} T - \frac{2694\cdot 2}{T},$$

we find

$$p = 3\cdot 67 \times 10^{-4} \quad \text{at} \quad 194^{\circ}\cdot 9 \text{ K.}$$

The vapour pressure of carbon dioxide has been measured down to  $90^{\circ}$  K. by Onnes and Weber †, their formula

$$\log_{10} p(\text{mm.}) = -\frac{1314\cdot 35}{T} + 1\cdot 75 \log_{10} T - 0\cdot 0019707T + 6\cdot 0508$$

gives

$$p = 5\cdot 29 \times 10^{-6} \quad \text{at} \quad 90^{\circ}\cdot 2 \text{ K.}$$

A correction to these values, due to Knudsen ‡, has to be applied in order to obtain the pressure which will be established in a vessel at room temperature connected to the trap. If  $p, T$  are the pressure and temperature in the trap,  $p', T'$  in the vessel at room temperature,

$$\frac{p}{p'} = \sqrt{\frac{T}{T'}}.$$

The correcting factor at  $194^{\circ}\cdot 9$  K. is 1·22, at  $90^{\circ}\cdot 2$  K. 1·79.

With a trap cooled in liquid oxygen it is not difficult to reach a pressure of  $10^{-6}$  mm. in a vessel which can be baked during exhaustion; the danger from carbon dioxide cannot therefore be as great as might have been anticipated. The limit of pressure easily obtainable with solid carbon dioxide is less well known, but it has been thought worth while to make a few rough measurements in order to ascertain more precisely what the effect of the presence of these substances is likely to be in an actual pumping system.

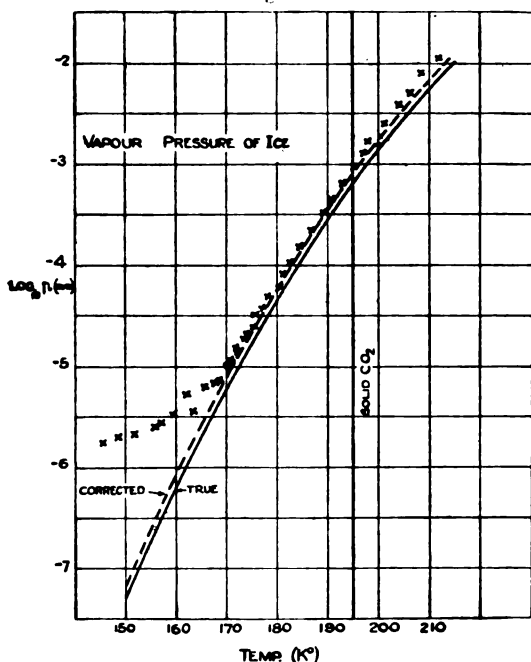
\* K. Scheel and W. Hause, *Ann. d. Phys.* xxix. p. 723 (1909).

† H. K. Onnes and S. Weber, *Kon. Akad. Wet. Amsterdam. Proc.* xvi. p. 445 (1913).

‡ M. Knudsen, *Ann. d. Phys.* xxxi. p. 205 (1910).

For this purpose an ionization gauge was pumped in the ordinary way through a cooled trap into which water or carbon dioxide could be admitted in known quantities. The filament of the gauge decomposes both these substances, and therefore alters the pressure when they are present; but since the pressure did not alter rapidly when the filament was heated, this source of error was immaterial for the present purpose. The gauge was calibrated against a McLeod gauge when filled with nitrogen, and Dushman's rule was used to apply this calibration to other substances.

Fig. 1.

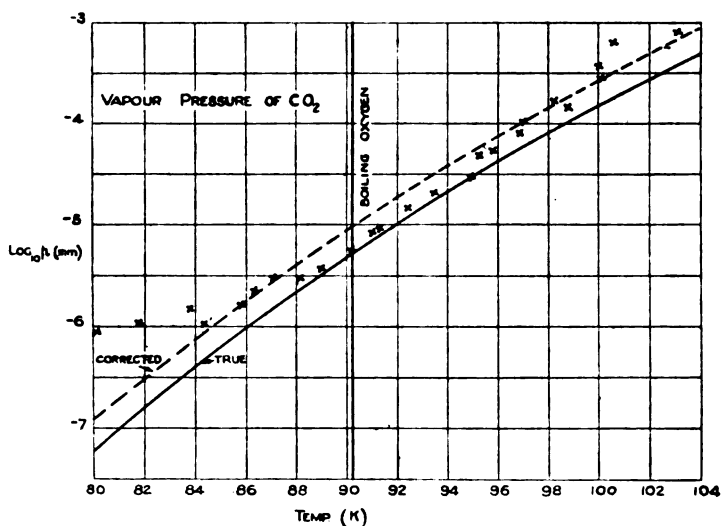


For temperatures above  $90^\circ\text{K.}$ , the trap was frozen in mercury in a Dewar flask by means of liquid oxygen, and the temperature allowed to rise naturally at the rate of about  $10^\circ$  an hour; for temperatures below  $90^\circ$ , the trap was immersed in liquid oxygen boiled at reduced pressure. The temperature was measured by a thermocouple.

The results of these measurements are shown in figs. 1 and 2, the points of which show the logarithm of the pressure in the gauge at various temperatures of the trap

into which carbon dioxide or water has been introduced. The full lines are the curves of Onnes and Weber and of Scheel and Hause, the dotted lines the corresponding values when Knudsen's correction is applied. At the higher pressures the divergence of the points from the dotted curve is not greater than can be accounted for by uncertainties in the calibration of the gauge and of the thermocouple; it is clear that the pressure in the gauge is determined, as it should be, by the vapour pressure of the condensed substance. But at the lowest temperatures,

Fig. 2.



the pressure in the gauge tends to a constant value much greater than the vapour pressure; there is a limit to the vacuum which can be reached independent of the substance condensed in the trap.

The existence of such a limit is, of course, characteristic of all evacuating systems; it is generally associated with gas present on the surfaces within the gauge or on the tubes connecting it with the pump; if suitable measures had been taken, the limit could doubtless have been considerably reduced. But the point important for our purpose is that, without any such measures, the limit is only about 1/10 of the pressure due to carbon dioxide in a trap at  $90^{\circ}2$  and only about 1/500 of that due to water in a trap at  $194^{\circ}9$ ; if traps at these temperatures

are used, these substances must be completely removed if they are not to set the limit to the pressure attainable. On the other hand, water need not be removed if liquid oxygen is used; and, if the trap is cooled to  $78^{\circ}$  K. (either by boiling the oxygen under reduced pressure or by using liquid nitrogen), the presence of carbon dioxide would not be harmful even if the pressure attainable in its absence was as low as  $10^{-7}$  mm.

There is another alternative conceivable: there may be a temperature above  $90^{\circ}$  at which the vapour pressure of carbon dioxide is so high that it is pumped away as quickly as a permanent gas, while that of water is so low that it is inappreciable. To discover whether there is such a temperature some observations were made on the time necessary to remove by pumping a known quantity of carbon dioxide introduced into the trap maintained at a known temperature. The results varied greatly, and in apparently similar experiments times in the ratio of 3 to 1 were obtained; probably the time depends on the distribution of the substance in the trap. If  $S$  is the volumetric speed of the pump,  $p$  the vapour pressure at temperature  $T$ , the time  $t$  required to remove a quantity of substance which would occupy a volume  $V$  at pressure  $p$  and temperature  $T$  should be given by

$$t = \frac{V}{S}.$$

If the time to remove the substance is identified with that required to make the pressure in the gauge begin to fall rapidly, it is of the same order as that calculated. On the other hand, the time to remove the substance completely, and to reach again the limiting pressure obtaining before the substance was introduced, is very much greater; for the initial rapid decrease corresponding to the volumetric speed is not maintained. The explanation is doubtless that some of the substance is absorbed on the glass and in that state possesses an effective vapour pressure very much less than that of the main portion. The amount of the gas so absorbed increases with the time that the glass is exposed to the gas; the practical question of importance is how high must the temperature of the trap be in order that a substance, admitted to it while the pump is acting, will be pumped away so quickly that it has no time to be absorbed and will therefore produce no permanent increase in the limiting pressure.

This question can be answered definitely only for an actual

piece of apparatus. The volume of our apparatus up to the cut-off was about 800 c.c.; the effective volumetric speed was 120 c.c. per sec. The admission to the trap of 0.1 c.c. of carbon dioxide or water (measured at N.T.P.) did not cause any permanent increase if the temperature of the trap was so high that the vapour pressure of the substance was at least 0.005 mm.; but if the vapour pressure was as low as 0.0005 mm., or, if 1 c.c. of the substance was admitted, some permanent increase was caused. Figs. 1 and 2 show that in the interval 108° K. and 150° K. the vapour pressure of carbon dioxide is above 0.005 mm. and that of water below  $10^{-7}$  mm. Consequently if the trap is kept at some temperature in this range, carbon dioxide will be removed as a permanent gas and water completely condensed; neither will exert a permanent pressure.

When carbon dioxide is likely to be present (water can hardly ever be avoided) and pressures of  $10^{-6}$  mm. have to be attained, there are then two alternatives. One is to use a colder trap; the other to use a warmer. Our experiments do not indicate that there is any ground for preferring one to the other, except in respect of ease of maintaining the necessary temperatures. In neither case are the difficulties serious. For the lower temperature liquid nitrogen can be used, but it is more expensive than liquid oxygen; an easier plan is to boil the oxygen at reduced pressure. All that is necessary for this purpose is to pass the trap into the Dewar flask through a rubber bung and to connect the interior to any rough vacuum. The evaporation of the liquid is not markedly more rapid than when the pressure is atmospheric. It is not even necessary to maintain continuously the connexion to the vacuum. When the pressure rises again to atmospheric, the liquid oxygen begins to boil at the surface, but unless the liquid is stirred vigorously, the lower layers will remain for a long time at the temperature to which they have been reduced by boiling at the reduced pressure. In a reasonably good Dewar flask, the temperature may be maintained at 80° K. by connecting the flask to the vacuum for a minute every half hour.

For the higher temperature there is no convenient constant temperature bath; but, since the range of temperature permissible is wide, none is needed. It is sufficient to fill a flask half full with mercury (interposing a layer of paper between the metal and the glass to reduce the chance of fracture) and to cool it by liquid oxygen poured



on the surface until the temperature, indicated by a copper-constantan couple connected to a pointer galvanometer, is within the desired range. To keep it within that range a little more oxygen has to be added every two or three hours.

It may be pointed out incidentally that the vapour pressure of carbon dioxide at  $90^{\circ}\cdot 2$  is a convenient rough standard for the calibration of ionization gauges, account being taken of the Knudsen correction.

LXX. *On the Quantitative Theory of Induction Heating.*  
By C. R. BURCH, B.A., and N. RYLAND DAVIS, B.A.\*

SUMMARY.

THIS paper investigates the energetics of an induction furnace, and discusses the conditions under which the transfer of energy from inductor to charge is maximal, and the influence of the various operating parameters on the "power factor" of the loaded inductor.

*Introduction.*

AN induction furnace—an apparatus in which conducting bodies may be heated by the eddy-currents produced in them under the influence of an alternating magnetic field—is already an indispensable piece of laboratory equipment, and is finding an ever-increasing application in commercial practice. Since Dr. Northrup's † paper, much has been written on the practical side of the subject, and formulæ have been developed determining the performance of an induction furnace; some of these are not too reliable.

The object of this paper is to develop a theory of the subject founded on sound physical reasoning, and some attempt at mathematical rigidity.

To crystallize our ideas, let us consider a thin annular charge, inductance  $L$ , resistance  $R$ , in an inductor  $L'$ ,  $R'$ , in which current (equal to the real part of  $Ie^{ipt}$ ) flows.

The current in the charge will then be denoted by the complex  $\frac{ipM}{R + ipL} Ie^{ipt}$ , where  $M$  is the mutual inductance between the charge and inductor.

\* Communicated by Prof. C. G. Darwin, F.R.S.

† E. F. Northrup, *Trans. Am. Electrochem. Soc.* vol. xxxv. (1919).

The rate of generation of heat in the inductor will be  $\frac{1}{2}R' |I|^2$ , and that in the charge,  $\frac{p^2 M^2 R |I|^2}{2(R^2 + p^2 L^2)}$ , where  $M$  is the inductor and charge.

The fraction of the total power supplied to the inductor, which appears as heat in the charge, will be called the "efficiency" of the inductor, and will be denoted by  $\eta$ .

It is 
$$\eta = \frac{p^2 M^2 R}{p^2 M^2 R + R'(R^2 + p^2 L^2)}.$$

We want  $\eta$  to be high, and it is a maximum if  $p$  is infinite. ( $L$ ,  $R$ ,  $L'$ ,  $R'$  are supposed independent of  $p$ .)

It behoves us to examine whether this frequency has any more obscure disadvantages. As regards the generator, its losses are proportional to the product of the R.M.S. current and R.M.S. voltage at its terminals, and in our simple case are proportional to the frequency, when this is high. We can annihilate the reactance of the inductor at a given frequency by placing in parallel with it a condenser of capacity given by

$$C = L_0 / [R_0^2 + p^2 L_0^2],$$

where

$$R_0 = R' + \frac{p^2 M^2 R}{R^2 + p^2 L^2} \quad \text{and} \quad L_0 = L' - \frac{p^2 M^2 L}{R^2 + p^2 L^2}$$

are the effective resistance and reactance of the loaded inductor. The generator need then only supply that part of the inductor current which is in phase with its voltage, the condenser supplying the power necessary to vary the energy stored magnetically by the system. This power, which is necessary to overcome the effective reactance of the inductor, is dynamically conserved, and its R.M.S. value will be termed "conserved power." The losses in the condenser (ohmic and hysteretic), though far smaller than the corresponding losses, in its absence, in the generator, are in practice appreciable, being proportional to the power which it conserves. Condensers capable of conserving high powers are exceedingly expensive; it may therefore be (and in general is) as important to obtain a low ratio of "conserved power" to charge heating as it is to obtain the highest possible ratio of charge heating to inductor loss. We can conveniently calculate the "conserved power" by the following method.

If the inductor voltage is represented by the real part of  $V' = V e^{ipt}$ , we can write

$$V' = |V| e^{i(pt+\gamma)}, \quad \dots \quad (\text{defining } \gamma)$$

$$I' = I e^{ipt} |V| \cdot \left[ \frac{R_0 - ipL_0}{R_0^2 + p^2 L_0^2} \right] e^{i(pt+\gamma)}.$$

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Now take

$$\tilde{V}' = |V| e^{-i(pt+\gamma)},$$

and form the complex product

$$\frac{1}{2} \tilde{V}' I' = \frac{1}{2} \left[ \frac{R_0 - ipL_0}{R_0^2 + p^2 L_0^2} \right] \cdot |V|^2.$$

This is independent of  $\gamma$  and  $t$ , and therefore

$$\tilde{V}' I' = \tilde{V} I.$$

Its real part is equal to the dissipated power, while its imaginary part determines the "conserved power." A sign convention is necessary, and we shall say

$$\left. \begin{aligned} P_d &= \text{real part of } \frac{1}{2} \tilde{V} I, \\ P_c &= \text{,, ,, ,, } \frac{1}{2} i \tilde{V} I. \end{aligned} \right\} \dots \dots (1)$$

That is to say, we shall consider the power conserved by an inductance as positive.

We can extend (1) to the case of a radially thick inductor and solid charge, as an integral:

$$\left. \begin{aligned} P_d &= \text{real part of } \frac{1}{2} \int_{r_1}^{r_2} \tilde{V}_r j_r dr, \\ P_c &= \text{,, ,, ,, } \frac{1}{2} i \int_{r_1}^{r_2} v_r j_r dr, \end{aligned} \right\} \dots \dots (2)$$

where  $v_r$  and the current density  $j_r$  may both depend on the radius.

We shall use (2) to define the effective resistance and reactance of the system in the following way:

$$\left. \begin{aligned} \frac{1}{2} |I|^2 R_0 &= P_d, \\ \frac{1}{2} |I|^2 p L_0 &= P_c. \end{aligned} \right\} \left( I = \int_{r_1}^{r_2} j_r dr \right) \dots \dots (3)$$

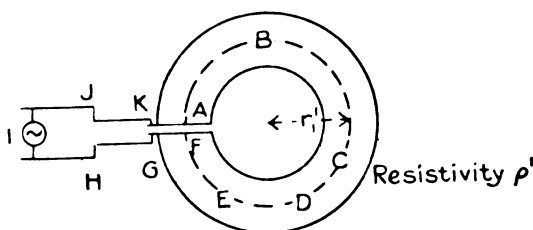
The radial distribution of current in the inductor is itself indeterminate without some specification of the type of generator connected thereto.

We shall therefore make the following stipulation:—

The inductor shall consist of one turn, complete, save for an infinitesimal gap, in which the condenser is placed (fig. 1).

The generator we assume connected to the perfectly conducting condenser plates A, F, and to be such that the current flowing in it and its leads produces no appreciable electric force, *qua* current, except in the region HIJ, and that the currents flowing in the inductor produce no electric force in the region GHIJK. Further, the magnetic field in the region HIJ shall be such that the line integral of the

**Fig. 1.**



total electric force,  $E_t$ , round GHIJ KG shall be  $V_t$ . The generator shall have no resistance. Then  $\int_F^A E_t ds$  ( $s=AF$ ) will, if the gap be sufficiently small, be independent of the position of the terminal points A, F, on the condenser plates. It is determined principally by the charges on the plates, and  $Lt \text{ gap} \rightarrow 0$  to a negligible extent by the part of  $E_t$  due to the currents, ABCDEF, *qua* currents, and will therefore be  $V_t$  for all terminal points, A, F, on the condenser plates.

*Notation.*

Total electric force at time $t$ .....	$E_t :$	
alternatively, real part of $E \epsilon^{ipt}$	$E.M.U.$	
Total magnetic force .....	$H_t :$	
alternatively, real part of $H \epsilon^{ipt}$	„	
Total magnetic induction .....	$B_t :$	
alternatively, real part of $B \epsilon^{ipt}$	„	
Generator voltage, at time $t$ .....	$V_t :$	
alternatively, real part of $V \epsilon^{ipt}$	„	
A certain change therein .....	$r_t :$	
alternatively, real part of $r \epsilon^{ipt}$	„	
Current density—inductor .....	$j_t' :$	
alternatively, real part of $j' \epsilon^{ipt}$	„	
Current density—charge .....	$j_t :$	
alternatively, real part of $j \epsilon^{ipt}$	„	

Pulsatance .....	$p$ radians sec. <sup>-1</sup> .
Time .....	$t$ sec.
Permeability—inductor, assumed unity.	
Permeability—charge .....	$\mu$ .
Resistivity—inductor .....	$\rho'$ E.M.U.
Resistivity—charge .....	$\rho$ "
Axial length—inductor .....	$l'$ cm.
Axial length—charge .....	$l$ "
Radius—inductor, outer .....	$R_2$ "
Radius—inductor, variably .....	$r_1'$ and $r'$ cm.
Radius—inductor, inner .....	$R_1$ cm.
Radius—charge, outer .....	$R$ "
Radius—charge, variably .....	$r_1$ and $r$ cm.
Radius—charge, inner assumed zero.	
Sign convention : $E, j, j'$ positive measured clockwise round	
	H +, or B +.

Parameters :

$$i = \sqrt{-1}, \quad \beta = \sqrt{\rho/4\pi ip\mu}, \quad \alpha = \sqrt{-\rho/4\pi ip\mu},$$

$$\beta' = \sqrt{\rho'/4\pi p}, \quad \alpha' = \sqrt{-\rho'/4\pi ip}.$$

With the above notation, we may write the first of Maxwell's equations in integral form as

$$\frac{d}{dt} \int_{(\sigma)} B_t d\sigma = - \int_{(s)} \rho j_t ds, \quad (0 < r_1 < R) \quad \dots \quad (4a)$$

the circuit  $s$ , enclosing the area  $\sigma$ , being in the charge, or

$$\frac{d}{dt} \int_{(\sigma)} B_t d\sigma = - \int_{(s)} \rho' j_t' ds - \nabla_t, \quad (R_1 < r_1' < R_2) \quad (4b)$$

$$(\sigma = \text{ABCDEA}) \quad (s = \text{ABCDE})$$

the circuit  $s$ , enclosing the area  $\sigma$ , now being in the inductor.

We shall further find it necessary to assume that the current density at a given radius is the same at all parts of the circumference. That is, we assume the frequency to be low compared with the gravest mode of free electrical oscillation of the inductor itself, in the absence of condenser or generator. The current will then be determined principally by the coefficients of inductance of the system, and to a negligible extent by the coefficients of capacity.

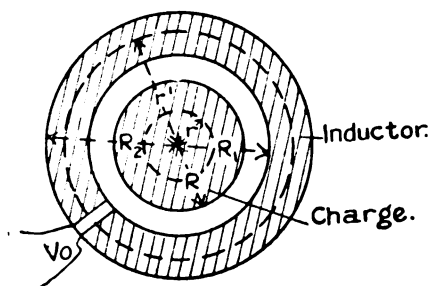
We may then write the second of Maxwell's equations as

$$\text{curl } H_t = 4\pi j_t, \dots \dots \dots (5)$$

the term  $+\frac{1}{c} \frac{dE_t}{dt}$  being, *a fortiori*, dropped, in view of the above frequency restriction.

To bring the problem within the sphere of tractable analysis we consider a cylindrical charge, long compared with its radius, placed coaxially in a long single-turn inductor. It will then be unnecessary to make any approximations regarding the distribution of current or flux that general theory might have suggested until the rigid solution has been written down—a procedure desirable in every analysis.

Fig. 2.



Considering the case of the loaded inductor, of which fig. 2 is a section, it will be seen that (5) can be written

$$\left. \begin{aligned} H_{r1t} &= 4\pi \int_{r_1}^R j_t dr + 4\pi \int_{R_1}^{R_2} j_t' dr', \quad (0 < r_1 < R_1) \\ H_{r1't} &= 4\pi \int_{r_1'}^{R_2} j_t' dr \quad (R < r_1' < R_2) \end{aligned} \right\} (6)$$

in integral form, and (4) becomes

$$\begin{aligned} \frac{d}{dt} \left[ 4\pi^2 \mu r_1^2 \int_{R_1}^{R_2} j_t' dr' + 4\pi^2 \mu \int_{r_1}^R j_t r_1^2 dr + 4\pi^2 \mu \int_0^{r_1} j_t r^2 dr \right] \\ = -2\pi \rho r_1 j_t \quad (0 < r_1 < R) \quad (7a) \end{aligned}$$

in the charge, while for the inductor we have

$$\begin{aligned} \frac{d}{dt} \left[ 4\pi^2 (\mu - 1) R^2 \int_{R_1}^{R_2} j_t' dr' + 4\pi^2 r_1'^2 \int_{r_1'}^{R_2} j_t' dr' + 4\pi^2 \mu \int_0^{r_1'} j_t r^2 dr \right] \\ = -2\pi \rho' r_1' j_t' + V_t. \quad (R_1 < r_1' < R_2) \quad (7b) \end{aligned}$$

The third integral on the L.H.S. of (7b), which represents the contribution due to the charge, to the total flux linking the ring  $r_1'$ , is independent of  $r_1'$ . The introduction of the charge can therefore be compensated by an addition to  $V$ , independent of  $r_1'$ , given by

$$v_t = \frac{d}{dt} \int_0^R \mu 4\pi^2 r^2 j_t dr + \frac{d}{dt} (\mu - 1) 4\pi^2 R^2 \int_{R_1}^{R_2} j_t' dr'.$$

In other words, if we circulate unit total current (per unit length)  $\left( \int_{R_1}^{R_2} j_t' dr' = 1 \right)$ , the loss in the inductor is not influenced by the presence of the charge, since the current density is, in both cases, the same function of the radius.

Representing all the electric quantities by complexes, we define the total current in a thick inductor (per unit length) as

$$I = \int_{R_1}^R j' dr, \quad \dots \quad (8)$$

we have from (2), since  $V$  and  $v$  are independent of  $r$ ,

$$\left. \begin{aligned} P_d &= \text{real part of } \frac{1}{2}(\tilde{V}I + \bar{v}I), \\ P_c &= \text{,, ,, ,, } \frac{1}{2}i(\tilde{V}I + \bar{v}I), \end{aligned} \right\} \quad \dots \quad (9)$$

We can now re-write (7a) and (7b) as

$$r_1^2 I + r_1^2 \int_{r_1}^R j dr + \int_0^{r_1} j r^2 dr = \frac{-\rho r_1 j}{2\pi i p \mu} \quad (0 < r_1 < R) \quad (10a)$$

and

$$\begin{aligned} 4\pi^2(\mu - 1)R^2 \int_{R_1}^{R_2} j' dr' + 4\pi^2 r_1^2 \int_{r_1'}^{R_2} j' dr' + 4\pi^2 \int_{R_1}^{r_1'} j' r'^2 dr' \\ + 4\pi^2 \mu \int_0^R j r^2 dr = -\frac{2\pi \rho' r_1' j' - V}{ip}; \quad (R_1 < r_1' < R_2). \quad (10b) \end{aligned}$$

For the empty inductor, (10b) becomes

$$4\pi^2 \int_{R_1}^{r_1'} j' r'^2 dr' + 4\pi^2 r_1'^2 \int_{r_1'}^{R_2} j' dr' = \frac{V}{ip} - \frac{2\pi \rho' j' r_1'}{ip}, \quad (10c)$$

the solution of which is

$$j' = \lambda \cdot J_1\left(\frac{r'}{\alpha}\right) + \nu Y_1\left(\frac{r'}{\alpha}\right), \quad \dots \quad (11)$$

where  $J_1$  and  $Y_1$  are Bessel functions of order unity and  $\lambda$  and  $\nu$  are chosen to satisfy (10) at the boundaries  $r_1 = R$ ,  $r' = R_2$ .

Substituting for  $j'$  and putting  $r' = R_1$ , we get

$$4\pi^2 R_1^2 \int_{R_1}^{R_2} \left\{ \lambda J_1\left(\frac{r'}{\alpha'}\right) + \nu Y_1\left(\frac{r'}{\alpha'}\right) \right\} dr' \\ = \frac{V}{ip} - \frac{2\pi\rho'}{ip} \cdot R_1 \left\{ \lambda J_1\left(\frac{R_1}{\alpha'}\right) + \nu Y_1\left(\frac{R_1}{\alpha'}\right) \right\},$$

i. e.

$$\alpha' 4\pi^2 R_1^2 \left[ \lambda \left\{ J_0\left(\frac{R_1}{\alpha'}\right) - J_0\left(\frac{R_2}{\alpha'}\right) \right\} + \nu \left\{ Y_0\left(\frac{R_1}{\alpha'}\right) - Y_0\left(\frac{R_2}{\alpha'}\right) \right\} \right] \\ = \frac{V}{ip} - \frac{2\pi\rho'}{ip} \cdot R_1 \left\{ \lambda J_1\left(\frac{R_1}{\alpha'}\right) + \nu Y_1\left(\frac{R_1}{\alpha'}\right) \right\},$$

which rearranges, since

$$J_2\left(\frac{R}{\alpha}\right) = -J_0\left(\frac{R}{\alpha}\right) + \frac{2\alpha}{R} J_1\left(\frac{R}{\alpha}\right),$$

and similarly for  $Y_2$ , as

$$\lambda R_1^2 \left\{ J_0\left(\frac{R_2}{\alpha'}\right) + J_2\left(\frac{R_1}{\alpha'}\right) \right\} + \nu R_1^2 \left\{ Y_0\left(\frac{R_2}{\alpha'}\right) + Y_2\left(\frac{R_1}{\alpha'}\right) \right\} \\ = \frac{V}{4\pi^2 ip \alpha'} \quad . \quad (12)$$

Putting  $r = R_2$  we have

$$4\pi^2 \int_{R_1}^{R_2} j' r'^2 dr' = \frac{V}{ip} - \frac{2\pi\rho'}{ip} \cdot R_2 \left\{ \lambda J_1\left(\frac{R_2}{\alpha'}\right) + \nu Y_1\left(\frac{R_2}{\alpha'}\right) \right\},$$

i. e.

$$\lambda \left\{ R_2^2 J_2\left(\frac{R_2}{\alpha'}\right) - R_1^2 J_2\left(\frac{R_1}{\alpha'}\right) \right\} + \nu \left\{ R_2^2 Y_2\left(\frac{R_2}{\alpha'}\right) - R_1^2 Y_2\left(\frac{R_1}{\alpha'}\right) \right\} \\ = \frac{V}{4\pi^2 ip \alpha'} + 2\alpha' R_2 \left\{ \lambda J_1\left(\frac{R_2}{\alpha'}\right) + \nu Y_1\left(\frac{R_2}{\alpha'}\right) \right\},$$

which also rearranges, giving

$$\lambda \left\{ R_1^2 J_2\left(\frac{R_1}{\alpha'}\right) + R_2^2 J_0\left(\frac{R_2}{\alpha'}\right) \right\} + \nu \left\{ R_1^2 Y_2\left(\frac{R_1}{\alpha'}\right) + R_2^2 Y_0\left(\frac{R_2}{\alpha'}\right) \right\} \\ = V/4\pi^2 ip \alpha' \quad . \quad (13)$$

Subtracting (13) from (12), we obtain

$$\lambda \cdot J_0\left(\frac{R_2}{\alpha'}\right) + \nu Y_2\left(\frac{R_2}{\alpha'}\right) = 0 \quad . \quad . \quad . \quad (14)$$



Writing  $J_0\left(\frac{R_2}{\alpha'}\right) + J_2\left(\frac{R_1}{\alpha'}\right) = a$

and  ~~$\frac{1}{2} \int_{R_1}^{R_2} \bar{V} j' dr'$~~   $Y_0\left(\frac{R_2}{\alpha'}\right) + Y_2\left(\frac{R_1}{\alpha'}\right) = b,$

and substituting (14) in (12), we find

$$\lambda \left\{ a - \frac{J_0\left(\frac{R_2}{\alpha'}\right)}{Y_0\left(\frac{R_2}{\alpha'}\right)} \cdot b \right\} = V/4\pi^2 ip \alpha',$$

or  $\lambda = \frac{V}{4\pi^2 R_1^2 ip \alpha' d} J_0\left(\frac{R_2}{\alpha'}\right), \quad \dots (15)$

$$\nu = \frac{V}{4\pi^2 R_1^2 ip \alpha' d} Y_0\left(\frac{R_2}{\alpha'}\right), \quad \dots (16)$$

where  $d = a Y_0\left(\frac{R_2}{\alpha'}\right) - b J_0\left(\frac{R_2}{\alpha'}\right),$

i. e.

$$\begin{aligned} d &= Y_0\left(\frac{R_2}{\alpha'}\right) \left\{ J_0\left(\frac{R_2}{\alpha'}\right) + J_2\left(\frac{R_1}{\alpha'}\right) \right\} \\ &\quad - J_0\left(\frac{R_2}{\alpha'}\right) \left\{ Y_0\left(\frac{R_2}{\alpha'}\right) + Y_2\left(\frac{R_1}{\alpha'}\right) \right\} \\ &= Y_0\left(\frac{R_2}{\alpha'}\right) J_2\left(\frac{R_1}{\alpha'}\right) - J_0\left(\frac{R_2}{\alpha'}\right) Y_2\left(\frac{R_1}{\alpha'}\right). \end{aligned}$$

Write

$$A = \bar{V}^2/4\pi^2 R_1^2 ip,$$

$\bar{V}^2$  being written for the time average of  $V^2$ , i. e.  $\left| \frac{V^2}{2} \right|$  (and similarly with  $\bar{I}^2$ ). Then (cf. treatment of the thin inductor, above)

$$\begin{aligned} \frac{1}{2} \int_{R_1}^{R_2} \bar{V} j' dr' &= -\frac{A}{d} Y_0\left(\frac{R_2}{\alpha'}\right) \left\{ -J_0\left(\frac{R_2}{\alpha'}\right) + J_0\left(\frac{R_1}{\alpha'}\right) \right\} \\ &\quad + \frac{\alpha A}{d} J_0\left(\frac{R_2}{\alpha'}\right) \left\{ -Y_0\left(\frac{R_2}{\alpha'}\right) + Y_0\left(\frac{R_1}{\alpha'}\right) \right\} \\ &= \frac{A}{d} \left\{ J_0\left(\frac{R_2}{\alpha'}\right) \cdot Y_0\left(\frac{R_1}{\alpha'}\right) - Y_0\left(\frac{R_2}{\alpha'}\right) \cdot J_0\left(\frac{R_1}{\alpha'}\right) \right\} \\ &= A \cdot \frac{J_0\left(\frac{R_2}{\alpha'}\right) \cdot Y_0\left(\frac{R_1}{\alpha'}\right) - Y_0\left(\frac{R_2}{\alpha'}\right) \cdot J_0\left(\frac{R_1}{\alpha'}\right)}{Y_0\left(\frac{R_2}{\alpha'}\right) \cdot J_2\left(\frac{R_1}{\alpha'}\right) - J_0\left(\frac{R_2}{\alpha'}\right) \cdot Y_2\left(\frac{R_1}{\alpha'}\right)}; \end{aligned}$$

. . . . . (17)

dividing top and bottom by  $J_0\left(\frac{R_1}{\alpha'}\right) \cdot Y_0\left(\frac{R_1}{\alpha'}\right)$ , we have

$$\frac{1}{2} \int_{R_1}^{R_2} \tilde{V} j' dr' = -A \cdot \frac{\frac{J_0\left(\frac{R_2}{\alpha'}\right)}{J_0\left(\frac{R_1}{\alpha'}\right)} - \frac{Y_0\left(\frac{R_2}{\alpha'}\right)}{Y_0\left(\frac{R_1}{\alpha'}\right)}}{\frac{J_0\left(\frac{R_2}{\alpha'}\right)}{J_0\left(\frac{R_1}{\alpha'}\right)} \cdot \frac{Y_2\left(\frac{R_1}{\alpha'}\right)}{Y_0\left(\frac{R_1}{\alpha'}\right)} - \frac{Y_0\left(\frac{R_2}{\alpha'}\right)}{Y_0\left(\frac{R_1}{\alpha'}\right)} \cdot \frac{J_2\left(\frac{R_1}{\alpha'}\right)}{J_0\left(\frac{R_1}{\alpha'}\right)}} \quad (18)$$

Since the inductor is made of copper ( $\rho' = 1.7 \times 10^9$ ) and is of necessity several centimetres in radius, the value of  $R_1'/\beta'$  at the frequency we contemplate (many thousand cycles per second) is of the order of several hundred. We may therefore write with considerable accuracy :

$$Y_2\left(\frac{R_1}{\alpha'}\right) / Y_0\left(\frac{R_1}{\alpha'}\right) = J_2\left(\frac{R_1}{\alpha'}\right) / J_0\left(\frac{R_1}{\alpha'}\right) = -1 + i\beta' \sqrt{2}(1+i) / R_1. \quad (19)$$

Again, since

$$R_1/\beta' \gg 1, \quad J_0\left(\frac{R_2}{\alpha'}\right) / J_0\left(\frac{R_1}{\alpha'}\right) \approx Y_0\left(\frac{R_2}{\alpha'}\right) / Y_0\left(\frac{R_1}{\alpha'}\right) \cdot e^{2(R_2-R_1)/\beta'}.$$

The inductor can always be made so thick that  $e^{2(R_2-R_1)/\beta'}$  is very large. We are therefore justified in writing

$$\frac{1}{2} \int_{R_1}^{R_2} \tilde{V} j' dr' = A / \{1 - i\beta' \sqrt{2}(1+i) / R_1\}$$

to an accuracy exceeding  $\{1 + e^{-2(R_2-R_1)/\beta'}\} : 1$

$$\begin{aligned} &= A \left\{ 1 + \frac{\beta' \sqrt{2}}{R_1} + \frac{\beta' \sqrt{2}}{R_1} \cdot i \right\} / \left\{ \left( 1 + \frac{\beta' \sqrt{2}}{R_1} \right)^2 + \frac{2\beta'^2}{R_1^2} \right\} \\ &= \frac{\bar{V}^2}{4\pi^2 \rho R_1^2} \left( \frac{\beta' \sqrt{2}}{R_1} - i \right), \quad \dots \quad (20) \end{aligned}$$

on neglecting  $2\sqrt{2}\beta'/R_1$  compared with unity and replacing  $A$ .

We therefore have for the power supplied to the empty inductor

$$\frac{\beta' \sqrt{2}}{4\pi^2 \rho R_1^3} \bar{V}^2 \text{ erg sec.}^{-1} \text{ cm.}^{-1}, \quad \dots \quad (21)$$

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and for the conserved power

$$\frac{1}{4\pi^2 p R_1^2} \bar{V}^2 \text{ erg sec.}^{-1} \text{ cm.}^{-1}. \quad (22)$$

the "power ratio," i. e.  $\frac{\text{Dissipated Power}}{\text{Conserved Power}}$ , being

$$\frac{1}{\sqrt{2\pi}} \cdot \frac{1}{R_1} \sqrt{\rho'/p}. \quad \dots \quad (23)$$

As the "power ratio" is small (seldom greater than  $10^{-2}$ ) we may take the inductor current as

$$\frac{\text{Conserved Power}}{V_0}, \quad \text{i. e. } \bar{I} = V/4\pi^2 p R_1^2,$$

and the error will seldom exceed one part in 20,000.

We can thus write (21) and (22) in terms of the inductor current  $I$  per unit length:

$$\frac{4\pi^2 R_1 \sqrt{p\rho'}}{\sqrt{2\pi}} \bar{I}^2 \text{ erg sec.}^{-1} \text{ cm.}^{-1} \quad \dots \quad (24)$$

and

$$4\pi^2 p R_1^2 \bar{I}^2 \text{ erg sec.}^{-1} \text{ cm.}^{-1} \quad \dots \quad (25)$$

We now calculate  $v$ , the necessary change in  $V$ , due to the introduction of the charge.

Reverting to equation (10a),

$$r_1^2 I + r_1^2 \int_{r_1}^R j dr + \int_0^{r_1} j r^2 dr = -\frac{\rho r_1 j}{2\pi i p \mu}, \quad (0 < r_1 < R)$$

the solution is

$$j = \frac{I}{\alpha} J_1\left(\frac{r}{\alpha}\right) / J_0\left(\frac{R}{\alpha}\right), \quad \dots \quad (26)$$

where

$$\alpha = \sqrt{-\rho/4\pi i p \mu}$$

and  $J_1$  and  $J_0$  are Bessel functions of the first and zeroth order.

Now

$$v = i p \mu \int_0^R 4\pi^2 r^2 j dr + (\mu - 1) i p 4\pi^2 R^2 I,$$

as has been noted.

Inserting the value for  $j$ , we get

$$\frac{1}{2} \bar{r} I = \left[ \frac{2\pi^2 \mu i \rho l}{\alpha J_0 \left( \frac{R}{\alpha} \right)} \cdot \int_0^R r^2 J_1 \left( \frac{r}{\alpha} \right) dr \right] I - (\mu - 1) i \rho 4\pi^2 R^2 \bar{I}^2 \quad (27)$$

$$= \left[ -4\pi^2 i \rho \mu I^2 \left[ R^2 - 2R\alpha J_1 \left( \frac{R}{\alpha} \right) / J_0 \left( \frac{R}{\alpha} \right) \right] \right] - (\mu - 1) i \rho 4\pi^2 R^2 \bar{I}^2, \quad (28)$$

$$\frac{1}{2} \bar{I}_{R_1}^{R_2} I = \frac{4\pi^2 \rho \mu \bar{I}^2}{\text{ber}^2 \frac{R}{\beta} + \text{bei}^2 \frac{R}{\beta}} \left[ 2\beta R \left( \text{ber} \frac{R}{\beta} \text{ber}' \frac{R}{\beta} + \text{bei} \frac{R}{\beta} \text{bei}' \frac{R}{\beta} \right) + i \left( R^2 + 2\beta R \left( \text{ber}' \frac{R}{\beta} \text{bei} \frac{R}{\beta} - \text{bei}' \frac{R}{\beta} \text{ber} \frac{R}{\beta} \right) \right) \right] - (\mu - 1) i \rho 4\pi^2 R^2 \bar{I}^2. \quad (29)$$

By [9] the real part of (29) gives the extra power absorbed by the inductor (carrying unit current), when the charge is inserted, and the coefficient of  $i$  in (29) taken negatively gives extra conserved power absorbed by the loaded inductor. (For unit current, this is its change of reactance.)

Two special cases of this formula are of interest: Firstly, when  $R/\beta$  approaches zero (and very approximately when  $R/\beta < 1$ ); secondly, when  $R/\beta$  approaches infinity (and very approximately when  $R/\beta > 3$ ).

*First Case.* ( $R/\beta < 1$ .)

In this case the expression for the power reduces to

$$2\pi^2 p^2 R^4 \frac{\mu^2}{\rho} \bar{I}^2 \text{ erg sec.}^{-1} \text{ cm.}^{-1}. \quad (30)$$

The expression (30) represents the well-known facts of low frequency induction, *e.g.* the heating of transformer cores. It will be noticed, however, that the criterion of its applicability is that  $R/\beta$  should be less than 1 and not that the frequency, *per se*, should be low. Actually, the parameters of the determining function are no fewer than four, *e.s.*  $\rho$ ,  $R$ ,  $\mu$ ,  $p$ . The looseness of the term "low frequency induction" is therefore apparent, and it is more reasonable to refer to this class of phenomena as "volume induction," since the criterion  $R/\beta > 1$  is tantamount to saying that the current density is proportional to the radius, *i.e.* the skin effect is not marked. Under these circumstances, the heating

is decreased in the ratio  $n:1$  if a charge consisting of one cylinder of radius  $R$  is divided into  $n$  cylinders of radius  $R/\sqrt{n}$ .

The conserved power in the charge (which, taken negatively, for unit current per unit length, is the inductor reactance abolished by the charge), is

$$4\pi^2 p R^2 (\mu - 1). \quad (\mu \gg 1) \quad . \quad . \quad (31)$$

If  $\mu = 1$ , the charge reactance is negligible compared with its resistance (both referred to the inductor).

*Second Case.* ( $R/\beta > 3$ .)

As in the first case, the criterion of applicability is not frequency alone.

We prefer therefore to refer to this condition as "surface" rather than "high frequency" induction heating, since when  $R/\beta > 3$ , the heat generation is confined substantially to the surface of the charge.

The power may be written

$$\bar{I}^2 2 \sqrt{2\pi} \cdot R \sqrt{p\mu} \text{ erg sec.}^{-1} \text{ cm.}^{-1}, \quad . \quad . \quad (32)$$

from which it follows that the effect of division of the charge, as above, is to increase the heating  $\sqrt{n}$  times.

The conserved power may be written

$$-4\pi^2 R^2 p \bar{I}^2. \quad . \quad . \quad . \quad . \quad . \quad (33)$$

It may be noted that Lt the ratio of power: conserved power  $\propto 1/\sqrt{p}$ , being in fact

$$\frac{1}{\sqrt{2\pi}} \cdot \frac{1}{R} \sqrt{\rho/p},$$

a result which, needless to say, contradicts Dr. Northrup's\* rather obscure statement that "when the frequency is sufficiently high to justify the assumptions" (which are not clearly stated) "the resistance of a charge is equal to its reactance."

We have seen that at the frequencies which we contemplate, the inductor loss varies as  $\sqrt{p}$ . ( $R_1/\beta \gg 3$ ). If in the charge ( $R/\beta < 1$ ), the efficiency is

$$\eta = p^2 R^4 \mu^2 l / \{ p^2 R^4 \mu^2 l + p \sqrt{2R_1} \sqrt{p\rho' l'} \}, \quad . \quad (34)$$

account being now taken of the different lengths of inductor

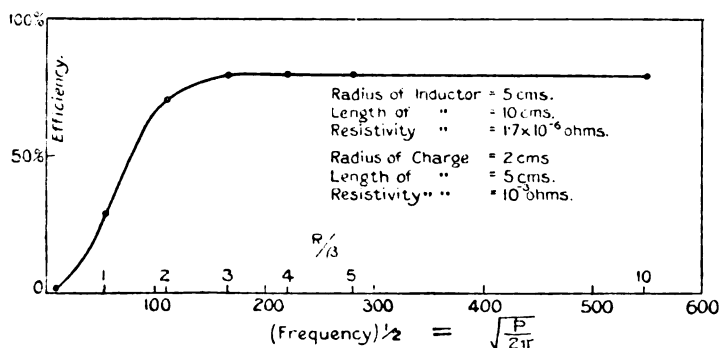
\* Northrup, *loc. cit.*

and charge.  $\eta$  may therefore be raised by raising the frequency until when  $R/\beta > 3$ , it becomes independent of frequency and is in fact

$$\eta = lR \sqrt{\rho} / \{lR \sqrt{\rho} + l'R_1 \sqrt{\rho'}\}. \quad (35)$$

The exact dependence of  $\eta$  on  $p$  is shown in the curve, fig. 3, the simple formula (21) being used for the inductor ( $R_1/\beta \gg 3$ ), while the rigid expression (29) is used for the charge.

Fig. 3.



It is clear, then, that the efficiency is maximal if  $R/\beta > 3$  in the charge. This implies  $R_1/\beta > 3$  in the inductor, since  $R$  cannot exceed  $R_1$ , and will in general be several centimetres less, moreover  $\rho$  will generally exceed  $\rho'$ . (The charge, even if of copper, will, let us hope, be hot.)

The fact that the necessary and sufficient criterion for maximal efficiency is  $R/\beta > 3$  in the charge, is a result of considerable interest, and universal application. It may theoretically be possible to improve on this maximal efficiency by winding the inductor with divided wire, though Professor Howe has shown\* that this must be used with a nice discrimination. He points out that when  $R_1/\beta'$  is large (it is always of the order of several hundred) and  $(R_2 - R_1)/\beta' > 3$ , multi-layer coils are definitely a mistake, and are in fact only justifiable if  $(R_2 - R_1)/\beta < 1$ .

In any case the difficulties of cooling a multi-layer inductor are very great, and actually the only practical form of inductor is a closely wound single-layer coil, of square copper tube, through which water may be circulated.

Considering such an inductor from the point of view of losses we are only interested in the thickness of the inner

\* G. W. O. Howe, J. I. E. E. lviii. p. 152 (1920); P. R. S., xciii. (1917).

wall, since it was shown that when  $(R_2 - R_1) / \beta' > 3$ , the losses are substantially independent of  $R_2$ . Taking 10,000 cycles as a minimum frequency, we find  $(R_2 - R_1)$  of the order of 1 mm. At one million cycles it would be of the order of  $\frac{1}{10}$  mm.

It will be of interest to consider the frequency which gives maximal heating in several special cases. For instance, consider a charge 3 cm. in radius and we should have for copper  $p > 1.5 \times 10^3 \text{ sec.}^{-1}$ , for carbon  $p > 4 \times 10^5 \text{ sec.}^{-1}$ , and for silicon  $p > 10^6 \text{ sec.}^{-1}$ . It is only when we have to heat very small charges of high resistivity that very high frequencies are desirable.

The effect of permeability affords interesting grounds for speculation. As in iron at high frequency the skin is extremely marked, hysteresis, which is a volume effect, should play a comparatively insignificant part. We must assume that the great efficiencies which are so easily obtained with iron below its magnetic change point must be accounted for almost wholly by its permeability. Experiments with iron indicated an average permeability of the order of 1000 at  $10^6$  cycles, a fact which seems to bear out the general observations of E. F. W. Alexanderson.

### *Choice of Frequency.*

Under almost all practical circumstances the frequency need not exceed  $10^4$  cycles/sec. and will in general be determined by the type of generator available. There is, however, one point worth noting in this connexion. The "power ratio" becomes proportional to the square root of the frequency, so that "conserved power" which the condenser is called upon to deal with will ultimately become at sufficiently high frequencies a matter of considerable concern, owing to ohmic loss in the electrodes and dielectric hysteresis. All things considered, therefore, it is desirable to work at frequencies exceeding by as little as possible that which makes  $R/\beta = 3$  in the charge.

### *Conclusions.*

It has been shown that there is a limit to the maximal efficiency of which an inductor coil is capable depending on its dimensions and on the dimensions and resistance of the charge; in the case of a cold copper charge, this maximal efficiency cannot exceed 50 per cent. It is further shown that the necessary and sufficient criterion for maximal efficiency is  $R/\beta > 3$  in the charge, and that while increase

of frequency generally allows of a smaller condenser capacity, at the same time it increases the conserved power.

The ultimate choice of frequency in any particular case must therefore rest on commercial considerations regarding the cost of condensers and generators subject only to the condition  $R/\beta > 3$  in the charge.

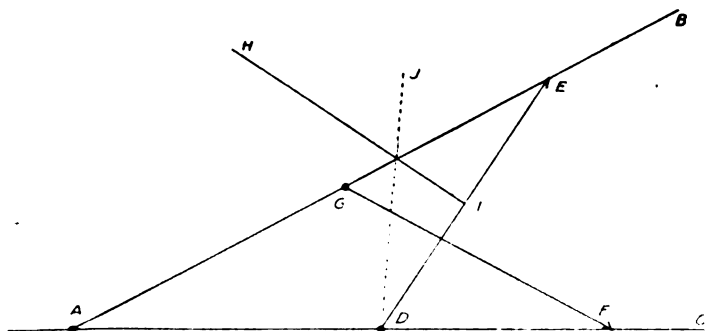
The authors wish to thank Professor C. G. Darwin, F.R.S., and Professor C. E. Inglis, M.A., M.I.C.E., for their kind encouragement and valuable criticism, and Mr. A. P. M. Fleming, C.B.E., M.I.E.E., Manager, Research and Education Departments, Metropolitan-Vickers Electrical Company Limited, for permission to publish this investigation.

Research Laboratories,  
Metropolitan-Vickers Electrical Co. Ltd.,  
Trafford Park, Manchester.  
November 21, 1925.

**LXXI. The Mechanical Solution of some Geometrical Problems.** By H. R. KEMPE, *M.Inst. C.E.\**

**A**S shown by fig. 1, AB and AC are two links linked together at A; GF is a link linked to AB at G, and

Fig. 1.



DE a similar link linked to AC at D; the ends of these links—E and F—slide on AB and AC respectively. Fixed to link DE and at right angles to it, at the midway point I, is a bar IH which can slide over AB.

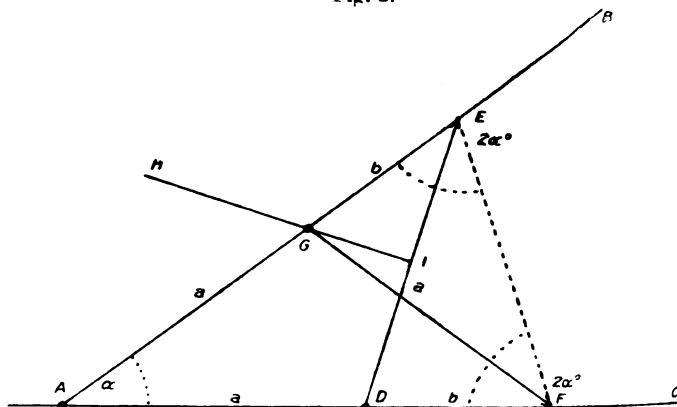
\* Communicated by the Author.



The lengths  $AD$ ,  $AG$ ,  $DE$ , and  $GF$  are all equal,  $HI$  may be any length.

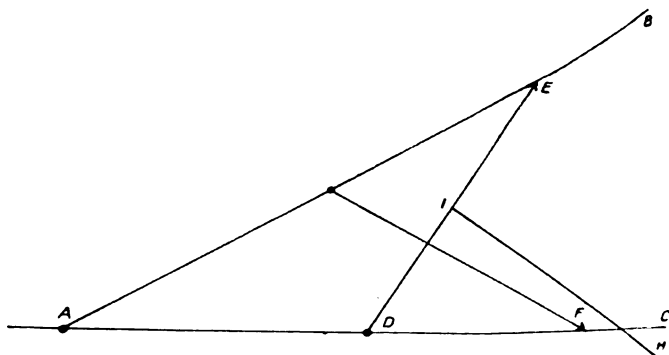
If, now,  $E$  and  $F$  be slid along  $AB$  and  $AC$  respectively, until  $HI$  comes on the point  $G$ , as shown by fig. 2, then the

Fig. 2.



triangle  $AEF$  will be formed, and this triangle will have each of the angles  $E$  and  $F$  to be *twice* the angle  $A$ , as in the case of Prop 10, Book IV, Euclid.

Fig. 3.



Now turn over the bar  $HI$ , as shown in fig. 3, and slide  $E$  and  $F$  along  $AB$  and  $AC$  respectively until the end  $F$  of

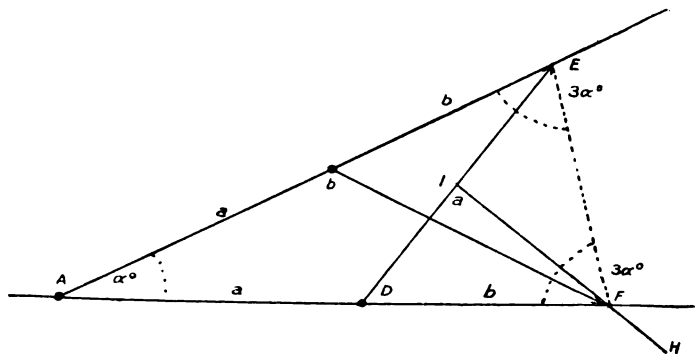
GF comes against HI, as shown by fig. 4, then triangle AEF will be formed, and this triangle will have each of the angles E and F to be *thrice* the angle A, a result which has no Euclidean solution.

It may be stated that in the case fig. 2,

$$\frac{b^2}{a} = a + b,$$

from which the ratio of  $a$  to  $b$  can be determined ; but in

Fig. 4.



the case, fig. 4,

$$\frac{a^2}{b^2} = \frac{2a + b}{a + b},$$

which is a cubic equation and cannot be solved by Euclidean geometry.

In reference to fig. 1 it may be mentioned that the angle JDE is one third of the angle JDC, so that the arrangement affords a means of trisecting an angle. To do this E would be slid along AB until the intersection of AB and HI comes on the line JD, JDC being the angle to be trisected ; this is practically the same solution as that which was given by the author in vol. xxvi. July 1918 of this Magazine.

Brockham, Betchworth,  
Surrey.

LXXII. *The Forces of Chemical Affinity. A Study of Crystal Structure in the Light of the New Atomic Models.* By ALBERT C. CREHORE\*.

SINCE the last paper† was communicated the general expression for the electrostatic force acting upon a first electron due to a second situated in any position whatever has been obtained. The so-called "circle-and-point" approximation to the oblate spheroid of the electron has been employed throughout. In that paper the discussion was limited to electrons having parallel axes, and this restriction of course prevented any consideration of crystal structure. General formulæ are required before a study of the grouping of atoms in a space lattice can be undertaken, because the axes of all electrons and of all atoms are not parallel to each other.

The process of finding the force upon a first atom due to a second atom is evidently merely one of summation after the force between individual electrons has been obtained—that is to say, summing the forces between the individual charges composing the atoms, taking one from each atom at a time. As between two hydrogen atoms each containing three individual bodies, two negative electrons and one positive charge of  $2e$ , this process requires  $3 \times 3 = 9$  expressions to be summed, while for two carbon atoms consisting of 15 charges each according to the model‡, fig. 3, twelve electrons and three positive charges of  $4e$  each, there are  $15 \times 15 = 225$  expressions to be summed. These expressions have been obtained both for two hydrogen atoms and for two carbon atoms in accordance with the models of these atoms, but their derivation is deferred for a subsequent communication. We are now concerned with their applications to crystal structure.

Although the crystal structure of solid hydrogen has never been experimentally determined, yet we shall give some space here to its consideration because the atom of hydrogen is far the simplest atomic form. It is hoped that this theoretical discussion may encourage those who have the laboratory equipment to undertake the X-ray examination of solid hydrogen, though the many difficulties are keenly realized, the work necessitating operations at very low temperatures.

\* Communicated by the Author.

† A. C. Crehore, Phil. Mag. May 1925, p. 839.

‡ A. C. Crehore, Phil. Mag. May 1922, p. 886.

There are many forms of space lattice in which different substances are known to crystallize, but there are four of them in particular that we shall consider both because of their common occurrence and their greater simplicity. These are (1) the simple cubic lattice, (2) the so-called face-centred cubic lattice, (3) the body-centred cubic lattice, and (4) two interpenetrating face-centred lattices such as the diamond.

In addition to the information afforded by the ordinary X-ray analysis of a crystal, which merely gives the locations of the centres of each atom, much more is required before any theoretical investigation of the electrostatic forces between the atoms can be undertaken. These depend fully as much upon the relative orientations of the axes of the atoms as upon their mutual distances. But the orientation of the axis of an atom depends primarily upon the electromagnetic forces due to the rotation of the fundamental charges within it, while it is only the translational forces that have a purely electrostatic character. In other words, as between two atoms there exists a mutual electromagnetic torque tending to bring their two axes into parallelism. The magnitude of this torque increases at first with an increase in the angle between their axes, and is in fact a function of this angle.

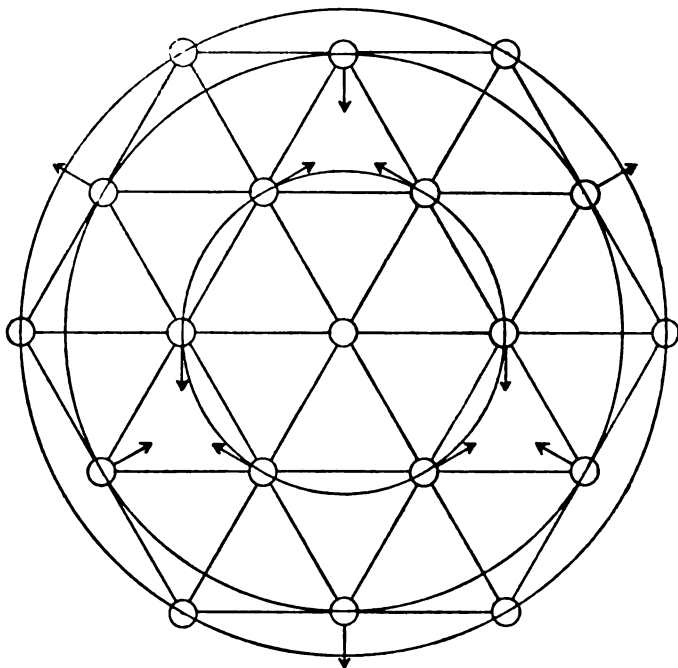
Although the form of atomic model now under discussion differs materially from that presented \* in 1915, yet in this matter of the turning moments of the force there is no essential difference. The centres of the electrons within the atoms in the models here discussed remain in stationary positions at the absolute zero of temperature, each merely rotating upon its own axis, while the electrons considered in that paper were supposed to revolve in orbits. In either case the rotation or the orbital revolution brings about the same result, a tendency to bring the two axes into parallelism. On p. 776 of the June paper referred to, the question of the equilibrium of turning moments of the forces in a lattice of atoms upon any selected atom is presented, and this reasoning applies with equal force to the new form of atom, being independent of the translational forces. In fact, from the standpoint of the moments of the forces alone it may be shown that the axes of the atoms can take but four different directions in any lattice belonging to the cubic system of crystals, namely parallel to the four diagonals

\* A. C. Crehore, Phil. Mag. June 1915, p. 750; Phil. Mag. Aug. 1915, p. 257.

of a cube, or to the four medial lines of a regular tetrahedron. The whole lattice is thereby divided into four equal groups of atoms, there being the same number having axes parallel to one medial line as to any other.

Moreover, each so-called (111) plane, one that is perpendicular to one of the diagonals of the cube, must have the axes of its atoms arranged as shown in fig. 2, p. 259 of the August 1915 paper referred to, which is also re-drawn

Fig. 1 A.

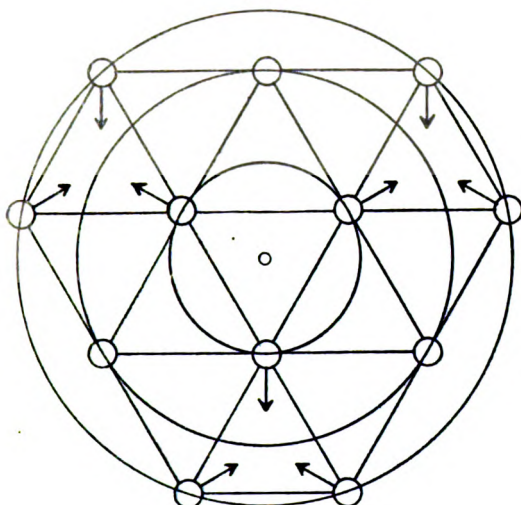


Showing the directions of the axes of the atoms in plane No. 0 of the simple cubic lattice. The small circles without arrows represent atoms with axes pointing upward perpendicular to the paper.

here as figs. 1 A, 1 B, and 1 C. The circles indicate axes pointing upward perpendicular to the plane of the paper, while the arrows represent axes pointing downward but projected on to the paper. These latter make an angle whose cosine is  $1/3$  with the downward perpendicular, or of  $-1/3$  with the upward perpendicular, that is to say with the axes of the atoms shown as plain circles. The cosine of the angle between any two axes or arrows in different

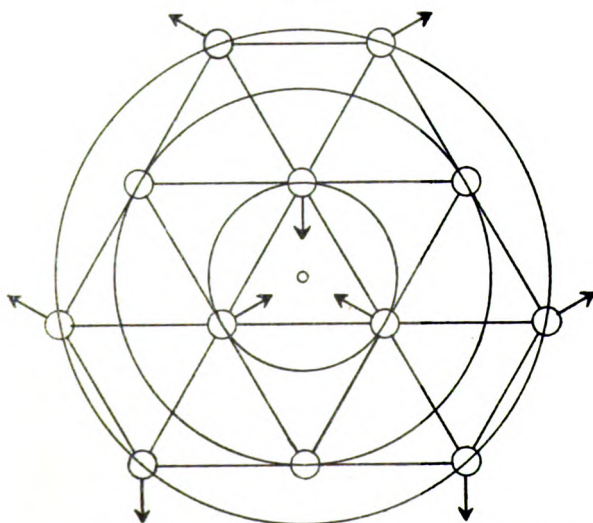
groups is then  $-1/3$ , so that  $\alpha = 109^\circ 28'3$ , the angle between any two medial lines of a regular tetrahedron.

Fig. 1 B.



Showing the directions of the axes of the atoms in plane No. 1 of the simple cubic lattice.

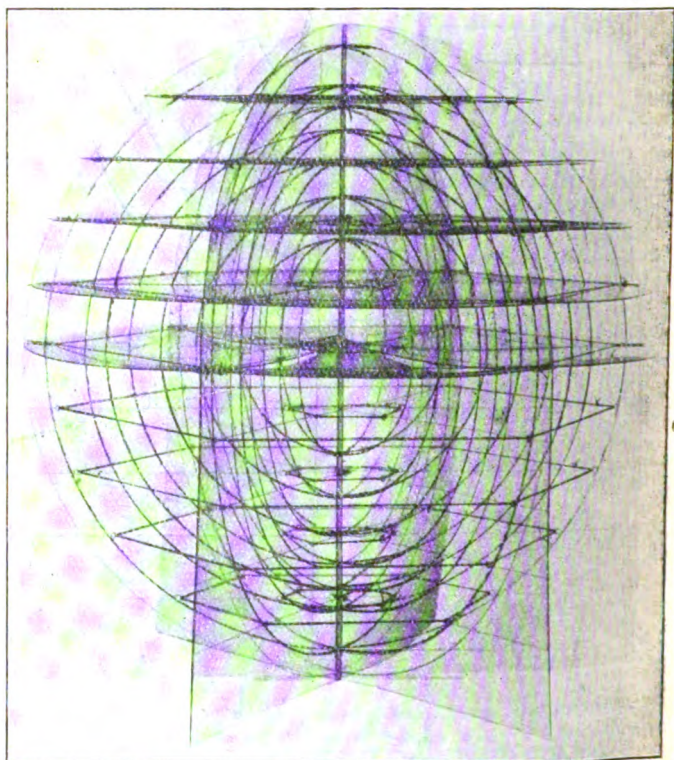
Fig. 1 C.



Showing the directions of the axes of the atoms in plane No. 2 of the simple cubic lattice.

In each of the four forms of cubic lattice above enumerated each (111) plane is in all respects like fig. 1A and like every other such plane. Consecutive planes cannot, however, always be brought into coincidence merely by moving the whole plane parallel to the cube diagonal. They must sometimes be shifted laterally, because the points of the equilateral triangles will sometimes fall upon the centres of those in a different plane.

Fig. 2 A.



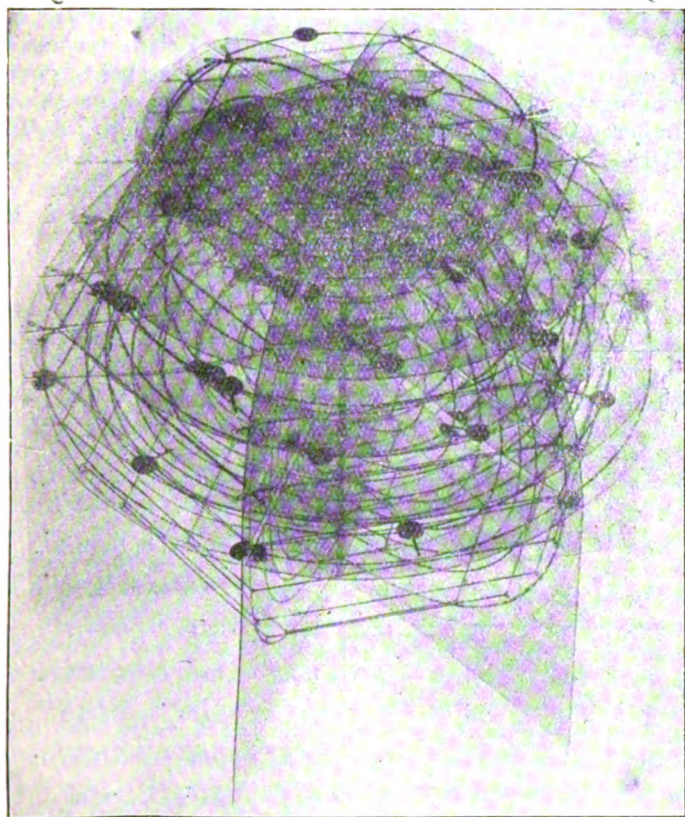
A side view of the model of the simple cubic lattice showing seven concentric spheres of atoms.

To represent all this in a model lattice requires more than is included in the models of lattices as at present constructed. A photographic reproduction of a model of a simple cubic lattice is shown in two different views in figs. 2A and 2B. It is made of sheets of transparent celluloid on which black



dots are drawn to indicate the atoms at the points of the lattice. Six vertical sheets set at  $60^\circ$  apart support the parallel (1 1 1) planes, which are equidistant, their separation being  $\frac{1}{3}$  the diagonal of the elementary cube, or  $\frac{1}{3}\sqrt{3}$  times the cube edge.

Fig. 2 B.



View of the model of the simple cubic lattice from a point which shows the elementary cubes.

About any selected atom of the lattice the neighbouring atoms are all arranged in several concentric spheres of increasing radii. Seven of these concentric spheres are contained in the model, their intersections with the six vertical planes being clearly shown by the seven concentric circles drawn on each vertical plane. The horizontal plane



through the selected atom at the centre of the spheres is the No. 0 plane, the first plane above it No. 1, the next No. 2, and so on. The top plane in the model is No. 4 containing atoms belonging to the 6th and 7th spheres only. The 5th sphere does not intersect this plane. Planes below the zero plane are numbered  $-1, -2$ , etc., but these have been omitted from the model. Each negative plane is, however, the counterpart of the positive plane with the corresponding number, being symmetrical with respect to the centre of the sphere, the directions of the axes at corresponding points being parallel to each other. The planes numbered 0, 1, and 2 of the model are shown as figs. 1A, 1B, and 1C above referred to.

TABLE I.  
Cubic Lattice.

PLANE 0. See fig. 1 A. $z=0$ .					
No. Sphere.	No. Circle.	No. Atoms.	$\cos \alpha$ .	$r'^2=r^2$ .	$r' = r$ .
0	0	1	1	0	0
2	1	6	$-1/3$	$2 l^2$	$\sqrt{2} l = 1.41421$
6	2	6	$-1/3$	6 „	$\sqrt{6} „ = 2.44949 „$
7	3	6	1	8 „	$2\sqrt{2} „ = 2.82842 „$
13	4	12	$-1/3$	14 „	$\sqrt{14} „ = 3.7417 „$
16	5	6	$-1/3$	18 „	$3\sqrt{2} „ = 4.2426 „$
21	6	6		24 „	$2\sqrt{6} „ = 4.8990 „$
23	7	12	$-1/3$	26 „	$\sqrt{26} „ = 5.0990 „$
	8	6	1	32 „	$4\sqrt{2} „ = 5.6569 „$
	9	12	$-1/3$	38 „	$\sqrt{38} „ = 6.1644 „$
$r' =$ radius circle. $r =$ radius sphere. $l =$ cube edge.					

In Table I. the second column gives the number of the circle in the zero plane including nine consecutive concentric circles, the third column gives the number of atoms in each circle, the fourth column the value of  $\cos \alpha$ , which

gives the angle that the axis of the given atom makes with the selected atom at the origin. Each atom in any one circle has the same value of  $\cos \alpha$ . The fifth column gives the square of the radius of the circle in terms of  $l$ , the edge of the elementary cube of the lattice as a unit, while the last column gives the radius itself.

Now there are certain spheres of atoms in the cubic lattice that include atoms occurring in the odd planes only, and that do not include any in the zero plane, and again there are spheres with atoms in other even planes that do not include any in the zero plane. Consequently the number of the sphere given in the first column counting from the smallest outwards increases faster than the number of the circle in the zero plane. The radius of the sphere is found from the radius of the circle by the formula

$$r^2 = r'^2 + z^2, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $r$  is the sphere's and  $r'$  the circle's radius, and  $z$  is the distance of the plane in question from the zero plane. For the zero plane, where  $z=0$ , the radii of sphere and circle are the same as shown in the last column of the Table. These radii in planes 0, 3, 6, etc. are computed from a centre at the point of one of the fundamental equilateral triangles in the plane, namely the selected atom; but in planes 1 and 2 the radii have to be computed from a centre at the centre of one of these fundamental triangles, instead of from its apex.

Table II. gives for plane 1 the data corresponding to that of Table I. Here, however, the radius of the sphere is greater than that of the corresponding circle because  $z$  is no longer zero. It may be remarked that  $\cos \alpha$  is the same for each atom in any one circle as before. No Table for plane 2 and other planes is required, because the radii of the circles in the plane as well as the values of  $\cos \alpha$  are the same for a circle of the same number as given in Table II. The sphere's radius must be computed, however, by the use of (1).

The cubic lattice is described with some completeness in Table III., including ten concentric spheres. The smallest sphere, No. 1, has a radius,  $l$ , equal to the cube edge and given in the second column. The angle,  $\alpha$ , is designated by the value of  $\cos \alpha$  in the third column. It has the value  $+1$  or  $-1/3$  in every case. Then follow in columns 4, 5, 6, and 7 the number of the (111) plane, the number of the circle in that plane, the number of atoms in that circle

and plane belonging to the sphere in question, and in column 7 the total number of atoms in that sphere.

TABLE II.  
Cubic Lattice.

PLANE 1. See fig. 1 B. $s = (\sqrt{3}/3)l$ ; $z^2 = (1/3)l^2$ .						
No. Sphere.	No. Circle.	No. Atoms.	$\cos \alpha$ .	$r'^2$ .	$r^2$ .	$r$ .
1	1	3	-1/3	$(2/3) l^2$	$l^2$	$l = 1.00000 l$
3	2	3	1	„ 4 „	3 „	$\sqrt{3}$ „ = 1.73205 „
5	3	6	-1/3	„ 7 „	5 „	$\sqrt{5}$ „ = 2.23607 „
8	4	6	-1/3	„ 13 „	9 „	3 „ = 3.00000 „
10	5	3	1	„ 16 „	11 „	$\sqrt{11}$ „ = 3.3166 „
12	6	6	-1/3	„ 19 „	13 „	$\sqrt{13}$ „ = 3.6056 „
15	7	3	-1/3	„ 25 „	17 „	$\sqrt{17}$ „ = 4.1231 „
17	8	6	1	„ 28 „	19 „	$\sqrt{19}$ „ = 4.3589 „
19	9	6	-1/3	„ 31 „	21 „	$\sqrt{21}$ „ = 4.5826 „
22	10	6	-1/3	„ 37 „	25 „	5 „ = 5.0000 „
	11	6	-1/3	„ 43 „	29 „	$\sqrt{29}$ „ = 5.3852 „
	12	9	-1/3	„ 49 „	33 „	$\sqrt{33}$ „ = 5.7446 „
	13	6	1	„ 52 „	35 „	$\sqrt{35}$ „ = 5.9161 „
$r^2 = r'^2 + z^2$ .						

The direction cosines X, Y, and Z are given in columns 8, 9, and 10, defining the position of the second atom with respect to the selected atom in terms of the  $i$ ,  $j$ , and  $k$  axes. Where a double sign is given, as for example in sphere 8, plane 3, circle 2,  $X = \pm \frac{1}{3}\sqrt{6}$ , the meaning is that of the six atoms in this circle three of them, or one half of them, have the positive and three have the negative sign. Where no double sign is indicated, each atom in the respective circle has the same direction cosine. But it should be

stated here that because of the manner in which the expressions for the forces have been derived the  $xi$ - and  $yj$ -axes each take three different positions in the horizontal (111) plane at angles of  $120^\circ$  apart, while the  $zk$ -axis alone remains fixed, being perpendicular to this plane. This is due to the fact that the direction of the  $yj$ -axis is defined by the vector  $k \times k'$ , where  $k$  is a unit vector along the axis of the selected atom and  $k'$  a unit vector along the axis of the given atom. The directions of the  $x$  and  $y$  axes are immaterial in getting the  $zk$ -component of the force. But the  $zk$ -component is the whole force because the  $xi$ - and  $yj$ -components evidently vanish for each and every circle in the lattice. In each case the sum of these forces for one circle of atoms gives three equal forces in the  $x, y$  plane at angles of  $120^\circ$  apart. These give a sum equal to zero. The  $zk$ -component is, therefore, the total force, and moreover, the axis of the atom always sets itself in the direction of this total force.

Column 11 of Table III. gives the product  $XZ$ , and column 12 the sum of these products for the sphere; while the last column gives the total number of atoms including all spheres. It will be shown that this product  $XZ$  is required for the purpose of summing the  $z$ -forces for the whole cubic lattice. We shall now make use of the expression for the force upon the positive charge of a first atom due to the whole of a single second atom situated in any position. The derivation of these expressions is given in a separate communication, so that some applications may be discussed here without unnecessary interruption. It has been proven that the force upon the positive charge of a hydrogen atom at the origin of coordinates due to the whole of a second hydrogen atom in any position is given by an infinite series of terms in  $r^{-3}$ ,  $r^{-4}$ , etc.,  $r$  being the distance between the centres of the atoms. The first term of the series is the  $r^{-3}$  term, and the whole force is given to a very close approximation indeed by the first two terms only of the series. The first term of this series is as follows:

$$F_z = \frac{e^2}{k} \{2(-3Z\zeta + \cos \alpha)Dr^{-3}\}, \dots \quad (2)$$

where  $\zeta$  stands for

$$\zeta = Z \cos \alpha - X \sin \alpha, \dots \quad (3)$$

and  $D$  for the quantity  $b_2 - b_1$  discussed in the last paper,  $b_2$  being the semi-minor axis of the upper electron and  $b_1$  that of the lower electron of the hydrogen atom.

TABLE III.—Cubic Lattice.

No. Sphere.	Radius sphere.	Cos $\alpha$ .	No. Plane.	No. Circle.	Atoms in circle.	Atoms in sphere.	X.	Y.	Z.	XZ.	$\Sigma XZ$ (Sphere).	Total No. Atoms.
1	$l$	$-\frac{1}{3}$	1	1	3	6	$\frac{1}{3}\sqrt{6}$	0	$\frac{1}{3}\sqrt{3}$	$-\frac{1}{3}\sqrt{2}$	$2\sqrt{2}$	6
$p^{-3}=1, \quad \Sigma(-3Zl+\cos\alpha)p^{-3}=3\sin\alpha p^{-3}\Sigma XZ=+8.$												
2	$\sqrt{2}l$	$-\frac{1}{3}$	0	1	6		0	$\pm 1$	0	0		
"	"	"	2	1	3	12	$-\frac{1}{3}\sqrt{3}$	0	$\frac{1}{3}\sqrt{6}$	$-\frac{1}{3}\sqrt{2}$	$-2\sqrt{2}$	
$p^{-3}=\frac{1}{4}\sqrt{2}, \quad \Sigma(\text{for sphere})=-2\sqrt{2}; \quad \Sigma(\text{total})=+5.17158.$												
3	$\sqrt{3}l$	1	1	2	3		$\frac{2}{3}\sqrt{2}$	0	$\frac{1}{3}$			
"	"	"	3	0	1	8	0	0	1			
$p^{-3}=\frac{1}{9}\sqrt{3}, \quad \Sigma(\text{for sphere})=0; \quad \Sigma(\text{total})=+5.17158.$												
4	$2l$	1	2	2	3	6	$\frac{1}{3}\sqrt{6}$	0	$\frac{1}{3}\sqrt{3}$			
$p^{-3}=\frac{1}{8}, \quad \Sigma(\text{for sphere})=0; \quad \Sigma(\text{total})=+5.17158.$												
5	$\sqrt{5}l$	$-\frac{1}{3}$	1	3	6		$-\frac{2}{15}\sqrt{30}$	$\pm\frac{1}{5}\sqrt{10}$	$\frac{1}{15}\sqrt{15}$	$-\frac{2}{15}\sqrt{2}$		
"	"	"	3	1	6	24	0			0	$-\frac{8}{5}\sqrt{2}$	
$p^{-3}=\frac{1}{25}\sqrt{5}, \quad \Sigma(\text{for sphere})=-\frac{32\sqrt{6}}{125}; \quad \Sigma(\text{total})=+4.59915.$												
												56

6	$\sqrt{6}l$	$-\frac{1}{3}$	0	2	6	$\pm 1$	0	$\frac{1}{3}\sqrt{3}$	0	$\frac{1}{3}\sqrt{2}$	$\frac{2}{3}\sqrt{2}$	0	$\frac{2}{3}\sqrt{2}$	$\frac{2}{9}\sqrt{2}$	$4\sqrt{2}$	80
	"	"	2	3	6	$\frac{2}{3}$										
	"	"	4	1	3	$\frac{1}{3}$	24	$\frac{1}{3}$	0							
	$p^{-3} = \frac{1}{36}\sqrt{6}, \quad \Sigma \text{ (for sphere)} = \frac{4}{9}\sqrt{6}; \quad \Sigma \text{ (total)} = +5.68781.$															
7	$2\sqrt{2}l$	1	0	3	6	1	0	0	0	0		0				
	"	"	4	2	3	$\frac{1}{3}\sqrt{3}$	12	0	$\frac{1}{3}\sqrt{6}$							
	$p^{-3} = \frac{1}{32}\sqrt{2}, \quad \Sigma \text{ (for sphere)} = 0; \quad \Sigma \text{ (total)} = +5.68781.$															92
8	$3l$	$-\frac{1}{3}$	1	4	6	$\frac{1}{9}\sqrt{6}$		$\frac{2}{3}\sqrt{2}$	$\frac{1}{9}\sqrt{3}$	$\frac{1}{3}\sqrt{2}$	$\frac{1}{27}\sqrt{2}$					
	"	"	3	2	6	$\pm \frac{1}{3}\sqrt{6}$		0	$\frac{1}{3}\sqrt{3}$	$\pm \frac{1}{3}\sqrt{2}$	$\pm \frac{1}{3}\sqrt{2}$					
	"	"	5	1	3	$-\frac{1}{9}\sqrt{6}$	30	0	$\frac{5}{9}\sqrt{3}$	$-\frac{5}{27}\sqrt{2}$	$-\frac{2}{3}\sqrt{2}$					
	$p^{-3} = \frac{1}{24}, \quad \Sigma \text{ (for sphere)} = -\frac{8}{81}; \quad \Sigma \text{ (total)} = +4.70015.$															122
9	$\sqrt{10}l$	$-\frac{1}{3}$	2	4	6	$-\frac{1}{15}\sqrt{15}$		$\pm \frac{2}{5}\sqrt{5}$	$\frac{1}{15}\sqrt{30}$	$-\frac{1}{15}\sqrt{2}$	$-\frac{1}{15}\sqrt{2}$					
	"	"	4	3	6	$-\frac{2}{15}\sqrt{15}$	24	$\pm \frac{1}{5}\sqrt{5}$	$\frac{2}{15}\sqrt{30}$	$-\frac{4}{15}\sqrt{2}$	$-4\sqrt{2}$					
	$p^{-3} = \frac{1}{100}\sqrt{10}, \quad \Sigma \text{ (for sphere)} = -\frac{4}{25}\sqrt{10}; \quad \Sigma \text{ (total)} = +4.1042.$															146
10	$\sqrt{11}l$	1	1	5	3											
	"	"	3	3	6											
	"	"	5	2	3		24									
	$p^{-3} = \frac{1}{121}\sqrt{11}, \quad \Sigma \text{ (for sphere)} = 0; \quad \Sigma \text{ (total)} = +4.1042.$															170

The use of the word upper means that electron on the positive side of the  $k$  or  $k'$  axes respectively. Eliminating  $\xi$  between (2) and (3) gives as the equivalent of (2)

$$F_z = \frac{e^2}{k} \{ 2 \cos \alpha (1 - 3Z^2) + 6XZ \sin \alpha \} (b_2 - b_1) r^{-3}. \quad (4)$$

Before proceeding to sum this expression for the whole cubic lattice, there are several points shown by Table III. which may be noted:—

1. The points of the cubic lattice, at each of which one atom is located, in any one sphere about any selected atom either lie all in the even or in the odd planes, but never in both even and odd.
2. The angle  $\alpha$  is the same for each atom in any one sphere,  $\cos \alpha$  being either  $-1/3$  or  $+1$  for any given sphere.
3. The sum of the quantity  $(1 - 3Z^2)$  taken for all the atoms in each and every sphere is zero, and consequently this sum is zero for the whole cubic lattice.
4. In those spheres where  $\cos \alpha = 1$ , the axes of the atoms being parallel to that of the selected atom,  $\sin \alpha = 0$ . Therefore the second term of (4) vanishes for all such spheres, and because the first term of (4) also vanishes for all such spheres because of the statement in 3 above, it follows that the sum of the expressions (4) vanishes for all spheres in the cubic lattice having parallel axes.

Table III. also gives the sum of the quantity that occurs in equation (2), namely  $(-3Z\xi + \cos \alpha)p^{-3}$ , for each individual concentric sphere of the cubic lattice as well as the total sum for all the spheres included in the table. Since  $r$  is different for different spheres it is put equal to  $pl$  so that the cube edge, which is a constant, may be factored out in taking the sum. Then  $p$  is defined as  $p = r/l$ , and  $p^{-3}$  is also given for each sphere.

Table IV. is an extension of Table III. to include thirty concentric spheres. To economize space the direction cosines have been omitted, but by the guidance of Table III. the reader will be able to supply them if desired to check the results in Table IV.

By writing

$$S = \Sigma (-3Z\xi + \cos \alpha) p^{-3}, \quad . \quad . \quad . \quad (5)$$

the summation being supposed to be extended over the

TABLE IV.  
Cubic Lattice.

No. Sphere.	Radius sphere.	$\cos \alpha$ .	Atoms in sphere.	Atoms, total.	$\Sigma(-3Z\epsilon + \cos \alpha)p^{-3}$ .		
					For sphere.		Total for Cubic Lattice.
					+	-	
1	1	$-\frac{1}{3}$	6	6	8.0000		+8.00000
2	$\sqrt{2}$ "	"	12	18		2.82842	5.17158
3	$\sqrt{3}$ "	1	8	26	0		"
4	2 "	1	6	32	0		"
5	$\sqrt{5}$ "	$-\frac{1}{3}$	24	56		0.57243	4.59915
6	$\sqrt{6}$ "	"	24	80	1.08866		5.68781
7	$2\sqrt{2}$ "	1	12	92	0		"
8	3 "	$-\frac{1}{3}$	30	122		0.98765	4.70016
9	$\sqrt{10}$ "	"	24	146		0.50597	4.19419
10	$\sqrt{11}$ "	1	24	170	0		"
11	$2\sqrt{3}$ "	1	8	178	0		"
12	$\sqrt{13}$ "	$-\frac{1}{3}$	24	202	0.36762		4.56180
13	$\sqrt{14}$ "	$-\frac{1}{3}$	48	250		0.087270	4.47453
14	4 "	1	6	256	0		"
15	$\sqrt{17}$ "	$-\frac{1}{3}$	48	304		0.093993	4.38054
16	$3\sqrt{2}$ "	$-\frac{1}{3}$	36	340	0.244431		4.62497
17	$\sqrt{19}$ "	1	24	364	0		"
18	$2\sqrt{5}$ "	1	24	388	0		"
19	$\sqrt{21}$ "	$-\frac{1}{3}$	48	436		0.285021	4.33995
20	$\sqrt{22}$ "	"	24	460		0.070479	4.26947
21	$2\sqrt{6}$ "	1	24	484	0		"
22	5 "	$-\frac{1}{3}$	30	514	0.074240		4.34371
23	$\sqrt{26}$ "	"	72	586	0.083552		4.42726
24	$3\sqrt{3}$ "	1	32	618	0		"
25	$\sqrt{29}$ "	$-\frac{1}{3}$	72	690	0.14838		4.57564
26	$\sqrt{30}$ "	"	48	738		0.084389	4.49125
27	$4\sqrt{2}$ "	1	12	750	0		"
28	$\sqrt{33}$ "	$-\frac{1}{3}$	36	786	0.030664		4.52192
29	$\sqrt{34}$ "	"	48	834		0.047474	4.47444
30	$\sqrt{35}$ "	1	48	882	0		"



whole of an infinite cubic lattice, it follows from (2) for the  $r^{-3}$  term only of the force that

$$F_z = \frac{e^2}{k} (2SD) l^{-3}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

since the displacement,  $D$ , must be the same for every atom. Including 30 concentric spheres comprising 882 atoms, Table IV. shows that the approximate value of  $S$  is

$$S = 4.474. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

An inspection of the last column of the Table shows the rapidity with which this summation approaches a limit for a larger number of spheres. For a very accurate value of  $S$  undoubtedly more spheres than 30 should be included. The radius of the thirtieth sphere is 5.9161 times the cube edge. The reason that these outlying spheres have any effect is the low order of the term, the inverse third power of the distance. The higher the order of the term the less spheres need be included. It follows from (6) and (7) that the sum of the forces of the whole lattice upon the positive charge of the selected hydrogen atom, so far as the  $r^{-3}$  atom is concerned and provided that hydrogen can form a simple cubic crystal in a stable form, is

$$F_z = \frac{e^2}{k} (8.949) D l^{-3}. \quad . \quad . \quad . \quad . \quad (8)$$

It will now be shown that (8) very approximately represents the whole force of the lattice upon the positive charge of one hydrogen atom, that is each hydrogen atom. This is because the  $r^{-4}$  term of the force-series vanishes for a cubic lattice and the higher order terms are small and negligible in any case. The complete expression for the force of a second hydrogen atom upon the positive charge of a first hydrogen atom including the  $r^{-4}$  term is, instead of (2), as follows :

$$F_z = \frac{e^2}{k} \{ 2f_1 D r^{-3} + 3f_2 (2b^2 - \rho a^2) r^{-4} \dots \}, \quad . \quad . \quad (9)$$

where  $f_1$  and  $f_2$  denote functions of  $X$ ,  $Y$ ,  $Z$ , and  $\alpha$  as follows :

$$f_1 = -3Z\zeta + \cos \alpha, \quad . \quad . \quad . \quad . \quad (10)$$

$$f_2 = 5Z\zeta^2 - Z - 2\zeta \cos \alpha, \quad . \quad . \quad . \quad (11)$$

where  $\zeta$  is given by (3).

For any lattice that is symmetrical with respect to a

centre, like the simple cubic lattice, and in which the atoms at each pair of corresponding points have parallel axes, as they have in the lattice described, the direction cosines are each reversed in sign for the second atom of such a pair. Now the function of  $X$ ,  $Y$ , and  $Z$  in the  $r^{-4}$  term of (9), namely (11), contains them only in an odd degree, and therefore the whole function merely changes sign for each pair of such atoms and cancels out completely in taking the sum for each pair and so for the whole lattice. This leaves the expression (8) as representing the whole force very approximately.

In the last communication the effect of the comparatively large internal forces acting within an atom in opposite directions upon positive and negative charges was discussed in some detail. For the hydrogen atom there are two constants,  $\rho_x$  and  $\rho_z$ , the former proportional to the lateral or equatorial displacement of the positive charge off from the centre line of the two electrons, and the latter to this quantity  $D = b_2 - b_1$ , which occurs in (8). The numerical value of  $\rho_z$  was determined in that paper to be  $30.7 \times 10^{24}$  derived from the property of the negative electron itself. In the present instance the equatorial force upon the positive charge of the atom is zero as above stated because of the property of the lattice, so that we do not require the constant,  $\rho_x$ . The force upon the positive charge in the axial direction is proportional to  $D$  and equal to

$$F_z = \frac{e^2}{k} (-\rho_z D) = -\frac{e^2}{k} (30.7 \times 10^{24}) D. \quad (12)$$

The reason for the negative sign given in the paper referred to should perhaps be repeated here. The force upon the positive charge is to be regarded as the cause of the displacement,  $D$ , so that it vanishes when the force vanishes, being proportional to the force for small displacements as they always are. Now  $b_2$  denotes the semi-minor axis of the electron on the upper side, that is on the positive side of the  $z$ -axis. If this electron has a larger minor axis than that of the lower electron, then  $D$  is a positive quantity. But it requires a negative force upon the positive charge, a downward force, and of course a positive force upon each electron to cause the compression of the lower and the expansion of the upper electron. That is to say, (12) requires the negative sign because the force is negative when  $D$  is positive, the constant,  $\rho_z$ , being essentially a positive quantity.

*The First Condition to be Satisfied by a Lattice.*

From this it becomes evident that the sign of equation (8), the total force of the lattice upon the positive charge, is wrong if it is to satisfy the required conditions for a stable cubic lattice. If  $D$  is positive this force is also positive, and a positive force cannot give rise to a positive value of  $D$ . Equations (8) and (12) should be expressions for the same force, but it is absurd to equate them because of the different signs. This constitutes a proof that the simple cubic lattice for hydrogen is not a possibility. By equating them we obtain a negative value for  $l$ , the cube edge, which is absurd. Overlooking, however, this absurdity for the moment, it is of some interest to note that the method in general does give a numerical value for  $l$ , even if absurd in this instance. We have

$$\frac{e^2}{k} (8.949) D l^{-3} = -\frac{e^2}{k} (30.7 \times 10^{24}) D, \quad \dots \quad (13)$$

whence  $l^{-3} = -3.43 \times 10^{24} \quad \dots \quad (14)$

and  $l = -0.663 \times 10^{-8} \text{ cm.} \quad \dots \quad (15)$

The legitimate conclusion is that hydrogen does not crystallize in the form of a simple cubic lattice, which has been used as a basis for equation (8). The writer is not aware that any of the so-called chemical elements crystallizes in the form of a simple cubic lattice. It seems to require at least two different kinds of atoms to form such a lattice, as for example sodium chloride, potassium chloride, or potassium iodide. In such crystals alternate (111) planes contain different kinds of atoms, and this gives a different resulting sum for the forces. It is now believed that this result, although worked out above on the basis of hydrogen alone, will prove to be true for the atoms of any other single element, and this investigation offers the reason why simple cubic crystals for the elements alone do not occur. This has been substantiated in the specific case of the carbon atom to be described below, and it is considered to be a general result. It is in complete agreement with experimental observations on crystals.

*The Face-centred Cubic Lattice.*

The next form of lattice to be treated is that of the so-called face-centred cubic lattice. A careful study of this lattice shows that the complete data for it may be

obtained directly from that of the simple cubic lattice above given. There are several points that will be noticed.

1. The (111) planes perpendicular to a cube diagonal are equally spaced at a distance of  $1/3$  the cube diagonal, namely  $\frac{1}{3}\sqrt{3}l$ , and in fact are spaced the same as the corresponding planes of the simple cubic lattice.

2. The edge of the elementary equilateral triangle, however, in each plane is one half as long as that of the triangle in the simple cubic lattice. In the cubic it is  $\sqrt{2}l$  and in the face-centred cubic  $\frac{1}{2}\sqrt{2}l$ .

3. Because of this difference in the size of the equilateral triangles the arrangement of the axes of the atoms in the corresponding (111) planes is also different. The zero plane in each lattice may be represented by fig. 1 A. In the simple lattice plane No. 1 must be like fig. 1 B, where the arrows of the central triangle point outward, and plane No. 2 like fig. 1 C, where they point inward, whereas in the face-centred lattice plane No. 1 must be like fig. 1 C, the arrows of the inner circle pointing inward, because this inner triangle forms a regular tetrahedron with the selected atom at the origin and all arrows point toward the centre of this tetrahedron. In a similar manner the inner triangle of plane No. 2 of the simple cubic forms a regular tetrahedron with the atom at the origin, but of twice the length of side, and all arrows point towards its centre.

4. Table V. gives the numbers of the planes in the cubic and face-centred lattices respectively that are arranged according to the three figures, 1 A, 1 B, and 1 C.

TABLE V.

No. plane.	Like fig. 1 A. Cubic or Face-centred.	Like fig. 1 B.		Like fig. 1 C.	
		Cubic.	Face-centred.	Cubic.	Face-centred.
	.....	.....	.....	.....	.....
9	7	8	8	7	
6	4	5	5	4	
3	1	2	2	1	
0	-2	-1	-1	-2	
3	-5	-4	-4	-5	
6	-8	-7	-7	-8	
.....	.....	.....	.....	.....	.....

5. Table VI. follows immediately from the correspondences in Table V. The numbers of the planes set opposite to each other in Table VI. are those in which the atoms are located in an identical manner including the directions of their axes.

TABLE VI.

No. plane.	Face-centred Lattice.	Simple Cubic Lattice.
	8	16
	7	14
	6	12
	5	10
	4	8
	3	6
	2	4
	1	2
	0	0

6. It follows from Table VI. that a face-centred lattice may be formed from a simple cubic lattice merely by omitting all of the odd planes of the cubic lattice, and then reducing the dimensions of the lattice by a factor of 2, because the edge of the equilateral triangle of the cubic is twice that of the face-centred lattice. Consequently the same computations made above for the simple cubic may now be used for the face-centred lattice, provided we substitute  $\frac{1}{2}l$  for  $l$ . In the  $r^{-3}$  term of the force-equation this makes  $l^{-3}$  eight times its former value.

7. By consulting Tables III. and IV. for the simple cubic lattice it will appear that when all of the odd planes are omitted the numbers of the concentric spheres that remain are given by the upper row of figures in Table VII. These spheres alone therefore constitute a face-centred lattice, some spheres having even and some odd numbers. The spheres may then be renumbered consecutively as in the lower row of figures. Sphere No. 10, for example, of the face-centred lattice is identical in all respects with sphere No. 18 of the simple cubic lattice when its dimensions are divided by 2.

TABLE VII.

## Numbers of Spheres.

Cubic .....	2, 4, 6, 7, 9, 11, 13, 14, 16, 18, 20, 21, 23, 26, 27, 29.
Face-centred ...	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16.

8. It is no longer true, however, that each sphere of the face-centred lattice embraces atoms either in odd or even planes, as was the case with the cubic lattice. This is because some of the even planes of the cubic receive an odd number in the face-centred lattice. The numbers of the spheres of the face-centred lattice that contain atoms in even, odd, or even and odd planes is given in Table VIII.

TABLE VIII.

	Even planes.	Odd planes.	Even and Odd planes.	
Sphere numbers,	4	1	3	11
Face-centred	8	2	5	13
Cubic Lattice.	12	6	7	14
	15	10	9	16

9. It still holds true, however, that  $\cos \alpha$  has the same value for each atom in any one sphere, being either  $-1/3$  or  $+1$ .

10. The face-centred lattice is also symmetrical about the centre, that is to say about any selected atom. Each atom is matched by another at the same distance on the opposite side of the centre, having its axis parallel to that of the given atom. The direction cosines  $X$ ,  $Y$ , and  $Z$  are each reversed in sign for the second atom of such a pair.

11. It follows from the statement in 10 that the sum of the  $r^{-4}$  terms of the force equation (9) will vanish for the face-centred lattice as they did for the cubic lattice, because the direction cosines occur in odd degrees only.

12. The sum of the forces according to (2) or (9) may, therefore, be found for the whole face-centred lattice by the use of Table IV. compiled for the simple cubic lattice by picking out those spheres only that form the face-centred lattice according to Table VII., and multiplying each sum by 8 for the reason above stated. This result is given in Table IX. The numbers given are, however, the same as for the cubic lattice in Table IV., the final result only being multiplied by 8 instead of the individual sums for each sphere.

For a face-centred cubic lattice, therefore, comprising 16 spheres embracing 428 atoms, we find

$$S = \Sigma(-3Z\xi + \cos \alpha)p^{-3} = -17.659. \quad \dots (16)$$

And according to (2) or (9) the whole force upon the positive charge of the single hydrogen atom at the centre

15

$$F_z = \frac{e^2}{k}(-35.32)Dl^{-3}. \quad \dots (17)$$

TABLE IX.  
Face-centred Cubic Lattice.

No. Sphere.	Radius sphere.	$\cos \alpha$ .	Atoms in sphere.	Atoms, total.	$\frac{1}{8}\Sigma(-3Z\zeta + \cos \alpha)p^{-3}$ .		
					For sphere.		Total for face-centred cubic lattice.
					+	-	
1	$\frac{1}{2}\sqrt{2}$ "	$-\frac{1}{2}$	12	12		2.82842	-2.82842
2	1 "	1	6	18	0		"
3	$\frac{1}{2}\sqrt{6}$ "	$-\frac{1}{2}$	24	42	1.08866		-1.30976
4	$\sqrt{2}$ "	1	12	54	0		"
5	$\frac{1}{2}\sqrt{10}$ "	$-\frac{1}{2}$	24	78		0.50597	-2.24573
6	$\sqrt{3}$ "	1	8	86	0		"
7	$\frac{1}{2}\sqrt{14}$ "	$-\frac{1}{2}$	48	134		0.087070	-2.33300
8	2 "	1	6	140	0		"
9	$\frac{3}{2}\sqrt{2}$ "	$-\frac{1}{2}$	36	176	0.244431		-2.08857
10	$\sqrt{5}$ "	1	24	200	0		"
11	$\frac{1}{2}\sqrt{22}$ "	$-\frac{1}{2}$	24	224		0.070479	-2.15905
12	$\sqrt{6}$ "	1	24	248	0		"
13	$\frac{1}{2}\sqrt{26}$ "	$-\frac{1}{2}$	72	320	0.083552		-2.07550
14	$\frac{1}{2}\sqrt{30}$ "	$-\frac{1}{2}$	48	368		0.084389	-2.15989
15	$2\sqrt{2}$ "	1	12	380	0		"
16	$\frac{1}{2}\sqrt{34}$ "	$-\frac{1}{2}$	48	428		0.047474	-2.20736
$\Sigma(-3Z\zeta + \cos \alpha)p^{-3} = -17.659.$							

Comparing this result with (8) for the simple cubic lattice it appears that the sign has changed and that the value is more than four times larger. As pointed out above, it is necessary that the sign be negative to satisfy the requirements. The simple cubic lattice would not answer for a single element because of the sign being wrong. As

before, we may now equate this new expression in (17) to (12) and find

$$-35.32Dl^{-3} = -30.7 \times 10^{24} D, \quad \dots \quad (18)$$

from which  $D$  cancels giving

$$l^{-3} = 0.87 \times 10^{24}; \quad l = 1.05 \times 10^{-8} \text{ cm.} \quad \dots \quad (19)$$

This result admits of the possibility that hydrogen may form face-centred cubic crystals, but it is by no means conclusive. The test has now advanced one step further than before without meeting with any obstacle. We might now turn to the experimental evidence contained in the density of solid hydrogen to see whether such a small value of the cube edge as found in (19) can possibly satisfy this density, but it seems a better plan to examine the second theoretical requirement to ascertain whether it too is satisfied.

*The Second Condition to be Satisfied by the Lattice.*

A second theoretical requirement that must be satisfied by any form of lattice is that the total force upon each and every atom in it shall be equal to zero in the condition of stable equilibrium. This involves a second equation which may next be given, the derivation of it being reserved for another paper. The total force of a second hydrogen atom in the position  $X, Y, Z, r$ , and  $\alpha$  upon a first hydrogen atom at the origin with axis along the  $zk$ -axis is as follows:—

$$\begin{aligned} F_z = \frac{3e^2}{k} \{ & f_3 D^2 r^{-4} \\ & + [f_4 l^2 D - \frac{1}{2}(f_5 + f_6) \rho a^2 D] r^{-5} \\ & + [5f_7 b^4 + \frac{5}{2}(f_8 + 2f_9) \rho a^2 b^2 - \frac{5}{2} f_{10} \rho^2 a^4] r^{-6} \}, \quad (20) \end{aligned}$$

where  $f_3$  to  $f_{10}$  are functions of  $X, Y, Z$ , and  $\alpha$  as follows:—

$$f_3 = 5Z^2 \zeta - 3Z \cos \alpha + X \sin \alpha, \quad \dots \quad (21)$$

$$\begin{aligned} f_4 = \cos \alpha (1 - \cos \alpha) (3 - 30Z^2 + 35Z^4) \\ + 10 \sin \alpha (\frac{1}{2} - \cos \alpha) XZ (3 - 7Z^2) \\ + \sin^2 \alpha [5(X^2 + Z^2) - 35X^2 Z^2 - 1], \quad \dots \quad (22) \end{aligned}$$

$$\begin{aligned} f_5 = 5XZ (3 - 7Z^2) \sin \alpha \\ + (3 - 30Z^2 + 35Z^4) \cos \alpha, \quad \dots \quad (23) \end{aligned}$$

$$\begin{aligned} f_6 = 2 - 10Z^2 - 5Y^2 + 35Z^2 (\xi^2 + Y^2) \\ - 10Z \xi \sin \alpha - 20XZ \sin \alpha \cos \alpha \\ + (2 - 15Z^2) \sin^2 \alpha - 5X^2 \cos^2 \alpha, \quad \dots \quad (24) \end{aligned}$$



$$\begin{aligned}
 * f_7 = & -63Z^3\xi^2 + Z(21X^2 - 7Z^2 - 3) \sin^2 \alpha \\
 & + Z(70Z^2 - 15) \cos^2 \alpha \\
 & + X(6 - 84Z^2) \sin \alpha \cos \alpha, \quad . \quad . \quad (25)
 \end{aligned}$$

$$\begin{aligned}
 f_8 = & -21Z\xi^2(1 - 3Z^2) + Z(3 - 7Z^2) \\
 & + 6\xi(1 - 7Z^2) \cos \alpha + 6Z \cos^2 \alpha, \quad . \quad . \quad (26)
 \end{aligned}$$

$$\begin{aligned}
 f_9 = & -(3 - 7Z^2)(Z + \xi \sin \alpha) \\
 & + 7Z(3Z^2 \sin^2 \alpha + 4XZ \sin \alpha \cos \alpha + X^2 \cos^2 \alpha) \\
 & + \frac{7}{2}Z(1 - 9Z^2)(\xi^2 + Y^2), \quad . \quad . \quad . \quad (27)
 \end{aligned}$$

$$\begin{aligned}
 f_{10} = & 3Z - 7Z(X^2 + 4Y^2 + \xi^2) + \frac{63}{2}Z(\xi^2 + Y^2)(X^2 + Y^2) \\
 & + 2\xi \sin \alpha [1 - \frac{7}{2}(X^2 + Y^2)] \\
 & + (Z \cos \alpha + 2X \sin \alpha - 14XZ\xi) \cos \alpha, \quad (28)
 \end{aligned}$$

where  $\xi = Z \sin \theta + X \cos \alpha$ .

The equation which is equivalent to (20) when the axes of the two hydrogen atoms are parallel to each other has already been published as (100) in the preceding paper †, and it will be found that this reduces to that when we put  $\sin \alpha = 0$ . The equatorial displacement,  $l$ , must also be put equal to zero in that equation in making the comparison, because it is assumed to be zero in (20) above. The equation is there quite fully discussed, and most of the essential points apply also to this more general expression. The striking characteristic is that the series begins with the  $r^{-4}$  term and need not include terms beyond the  $r^{-6}$  term. The  $r^{-4}$  term contains  $D^2$  as a factor, the  $r^{-5}$  contains  $D$ , while the  $r^{-6}$  term contains the fourth degree of  $a$  and  $b$ ,  $a$  being the radius of the circle in the circle-and-point electron and  $b$  its semi-minor axis. If we make  $D=0$ , the  $r^{-4}$  and  $r^{-5}$  terms vanish and no equilibrium would be possible. It requires the presence of these three terms to fulfil the conditions of an equilibrium.

Let us now consider a single pair of atoms of either the cubic or face-centred lattices at equal distances on opposite sides of the selected atom and having axes parallel to each other. Equal values of  $f_3$  in (21) but with opposite signs are obtained for this pair of atoms because  $X$  and  $Z$  occur in each term in an odd degree. Hence the sum of these functions for the pair of atoms is zero. It is, therefore, zero for the whole lattice, and the  $r^{-4}$  term drops out from the equation. The  $r^{-5}$  term does not vanish, but the  $r^{-6}$

\* Since the paper went to press it has been proved that  $f_7 = -f_6 = -2f_{10}$ .  
A. C. Crehore, Phil. Mag. May 1925, p. 868.

term vanishes for a similar reason to that given for the  $r^{-4}$  term, because X, Y, and Z occur in odd degrees in each term of the functions  $f_7, f_8, f_9$ , and  $f_{10}$ .

This furnishes conclusive proof that the sum of the forces (20) written for each atom in the lattice cannot be set equal to zero, for the coefficient of the  $r^{-5}$  term does not vanish, and no adjustment of the size of the cube edge is possible that will make the whole force vanish and produce a stable condition of equilibrium.

The above reasoning rules out any form of lattice for hydrogen that is symmetrical with respect to a centre. This generalization extends the proof so as to exclude the third form of lattice above enumerated, the body-centred cubic lattice, which has not been given in detail. It is thus easier to say what the form of the crystal of solid hydrogen is not than to construct what it is, but even so, results such as these have a practical value that is far from negative. It seems best at this stage to give some consideration to the carbon atom before resuming the discussion of hydrogen.

### *Carbon.*

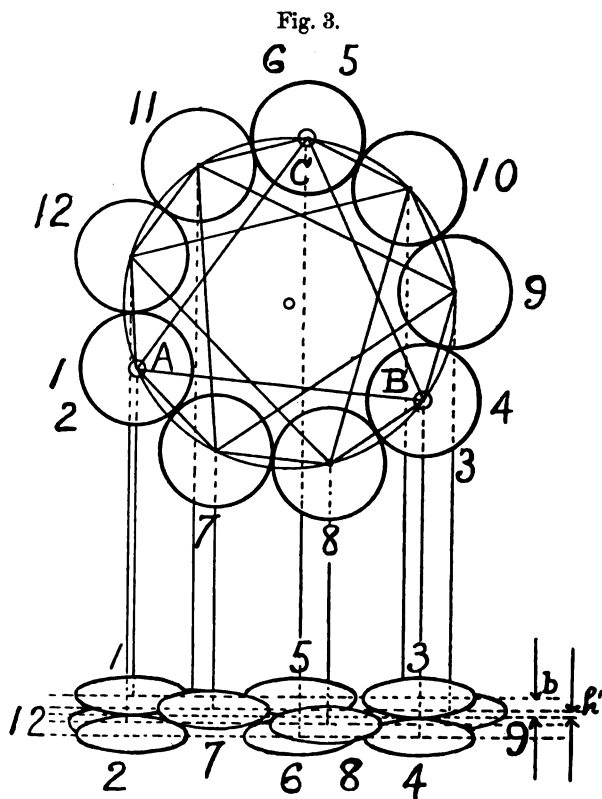
The model of the carbon atom that we shall use for purposes of computation was first published in the *Philosophical Magazine* for May 1922, shown in fig. 1, p. 887, and described on p. 890. Some changes\* have been made in some of the other atoms shown at that time in this figure but not in that of carbon, which is shown here in fig. 3 in two views—an axial and an equatorial view.

One of the reasons for choosing carbon for investigation here is that there are no isotopes known for carbon, and this is certainly not true for lithium and probably not for glucinum and boron, the next atoms in order of atomic number, excepting helium that forms no compounds. Another reason is the perfect symmetry of the model of the atom, the fact that it has the form of a ring containing three alpha-particles and no hydrogen atoms, and that there exist at least two crystals, the diamond and graphite, with which theoretical results may be compared and checked. And, again, carbon forms many compounds with hydrogen, which may ultimately be worked out in some detail when there has been a satisfactory confirmation of the theory by the use of crystals.

The three positive charges, A, B, and C of fig. 3, in the three alpha-particles of the carbon atom form a perfect equilateral

\* See fig. 2, p. 37, 'The Progress of Atomic Theory,' A. C. Crehore.

triangle in the equatorial plane of the atom. There are then twelve negative electrons, six of them, 1-6, belonging to the alpha-particles, and six, 7-12, serving as the so-called connecting electrons to bind the structure together. There are thus four perfect equilateral triangles of negative electrons,



Detail drawing of the Carbon atom in plan and elevation, showing the distances  $b$  and  $h$ .

the upper ones, 1, 3, and 5, in the alpha-particles forming the first, the lower ones, 2, 4, and 6, the second, the upper three connecting electrons, 7, 9, and 11, the third, and the lower three, 8, 10, and 12, the fourth triangle. The connecting electrons are supposed to be staggered alternately up and down all around the ring; that is to say, they are not exactly in the equatorial plane, but located at about half the distance

from it that the electrons in the alpha-particles have. The reason for this separation from the equator is the mutual repulsion of the adjacent negative connecting electrons. This repulsion is balanced, however, by the strong attraction they have for the alpha-particles, each having an effective charge of  $+2e$ .

In the free carbon atom the common distance of all electrons in the alpha particles from the equator is the same, equal to  $b$ , the semi-minor axis of the negative electron very approximately. Similarly the connecting electrons have the same distance from the equator, the one as the other, say equal to  $h'$ , which differs from  $b$  and is thought to be about half the value of  $b$ . When the atom forms part of a molecule, however, instead of being free, the upper distances,  $b$  and  $h'$ , change to  $b_2$  and  $h_2'$ , and the lower distances are  $-b_1$  and  $-h_1'$ , each of which differs by a very small amount from  $b$  and  $h'$ . The differences,  $D = b_2 - b_1$  and  $H = h_2' - h_1'$ , which are zero in a free atom, become appreciable when a molecule is formed. A finite value for  $D$  is in fact demanded in order that a molecule may be formed.

The expression for the force that has been derived from the electrostatic forces for a second such carbon atom acting upon the positive charge only of the first carbon atom at the origin of coordinates, the axis of the latter coinciding with the  $z$ -axis, is as follows:—

$$F_z = \frac{e^2}{k} \left\{ 36 f_1 (D + H) r^{-3} + 108 f_2 [(b^2 + h'^2) - \rho a^2] r^{-4} \dots \right\}, \quad (29)$$

$\begin{matrix} C_2 \text{ on} \\ 3 \text{ positive charges} \\ \text{of first atom.} \end{matrix}$

where the functions,  $f_1$  and  $f_2$ , are identical with those determined in the case of hydrogen given above by (10) and (11). The corresponding expression for hydrogen was given in (9). If in (29) we should make  $h' = b$  and  $H = D$ , then it is seen that the force becomes exactly 36 times that of (9), 36 being the square of the atomic number of carbon. But  $h'$  is not equal to  $b$ , nor  $H$  to  $D$  in the carbon atom, and it is here that the character of the expression for carbon differs from that for hydrogen. Otherwise we might form the same conclusions from this equation that were drawn from (9) for hydrogen.

Without making any use of (29) for the moment, let us pass immediately to the second condition which must be satisfied by any form of lattice structure. For this we require the force of a second carbon atom upon the whole

of the first atom at the origin. This has been proven to be as follows:—

$$F_z = \frac{e^2}{k} \left\{ 27f_3(D+H)^2r^{-4} \right. \\ \text{Second} \quad + 27[f_4(b^2+h'^2) - f_5\rho a^2 - f_6\rho a^2](D+H)r^{-5} \\ \text{carbon atom} \\ \text{on first} \\ \text{carbon atom.} \quad + 135[f_7(b^2+h'^2)^2 + (f_8+2f_9)\rho a^2(b^2+h'^2) \\ \left. - 2f_{10}\rho^2 a^4\right]r^{-6} \dots \}, \quad (30)$$

where the functions  $f_3$  to  $f_{10}$  are given by (21) to (28), being identical with those obtained in the case of hydrogen.

Here also it is seen that, if  $h'=b$  and  $H=D$ , equation (30) is exactly 36 times (20), the corresponding expression for hydrogen. But this is not true, a fact which gives rise to some differences between the two equations. However, because the functions  $f_3$  to  $f_{10}$  are the same as before, we find that, when the forces of a single pair of atoms on opposite sides of the selected atom at the same distance and having parallel axes are added together, both the  $r^{-4}$  and the  $r^{-6}$  terms of (30) vanish, leaving only the  $r^{-5}$  term. As pointed out above, this proves conclusively that no form of lattice having a centre of symmetry can satisfy the condition that the sum of the forces for the lattice shall be zero. From this it follows that carbon will neither crystallize in the form of a simple cubic lattice, a face-centred cubic, nor a body-centred cubic lattice. This conclusion is undoubtedly true, the structure of both the diamond and graphite being different from the lattices named.

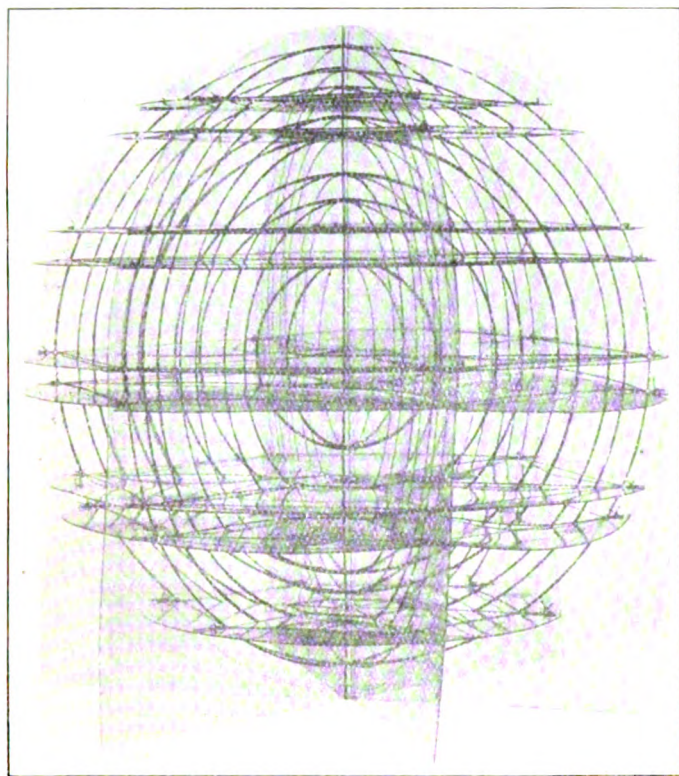
There is a double reason why the simple cubic lattice will not answer, namely that neither the first nor the second condition is satisfied, the first condition involving the sum of equations like (29) for the lattice, and the second like (30). The sum of (29) comes out positive for the cubic lattice, whereas it must be negative as pointed out. The sum of (30) must be zero, and this condition cannot be satisfied. On the other hand, the face-centred cubic lattice satisfies the first condition, since the sum of (29) is negative as shown. The sum of (30), however, cannot be zero.

Now it is well known that there are a number of elements which crystallize as a face-centred lattice. It may be presumed, therefore, that the fundamental equation for such elements corresponding to (30) will contain in the  $r^{-4}$  and  $r^{-6}$  terms functions of  $X$ ,  $Y$ , and  $Z$  including a constant term that does not change sign by a reversal of their signs. Aluminium is an example of an element that forms a face-centred lattice, and aluminium happens to be the atom of highest atomic number for which a model has been

constructed. It can already be seen from its model that such terms as referred to make their appearance in the case of aluminium, and we may expect that this second condition that is not satisfied by carbon will be fulfilled by aluminium, thus allowing the formation of the face-centred lattice. But the case of aluminium is not completed, and no more can be stated here than that it seems probable that it will yield a face-centred lattice.

*The Diamond Lattice.*

Fig. 4 A.

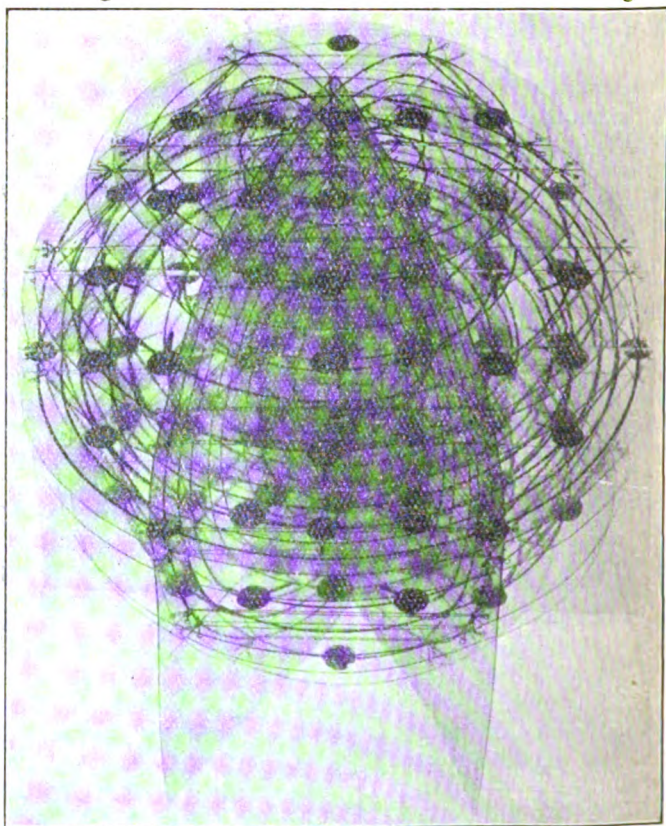


Side view of the model of the Diamond Lattice, showing eight concentric spheres of atoms.

A model of the diamond lattice constructed along the same lines as that of the simple cubic lattice above described and shown in figs. 2 A and 2 B is pictured in figs. 4 A

and 4 B in two different views. This lattice consists of two interpenetrating face-centred cubic lattices displaced along the direction of the diagonal of the cube by a distance from each other of  $\frac{3}{4}$  the altitude of the regular tetrahedron, whose base is one of the elementary equilateral

Fig. 4 B.



View of the model of the Diamond Lattice from a point which shows the cubical structure.

triangles. There are nine of the (111) planes shown in the model, which include 98 atoms in 8 concentric spheres surrounding the selected atom. A scheme for this lattice is shown in Table X. The first column gives the number of the (111) plane, and the second column the distance of

TABLE X.

## Diamond Lattice.

No. Plane.	$z$ of plane.	Like Fig. 1 A.	Like Fig. 1 C.	Like Fig. 1 B.
-8	$-\frac{4}{3}\sqrt{3}l$			"
-7	$-\frac{13}{12}\sqrt{3}l$			"
-6	$-\sqrt{3}l$	"		
-5	$-\frac{3}{4}\sqrt{3}l$	"		
-4	$-\frac{2}{3}\sqrt{3}l$		"	
-3	$-\frac{5}{12}\sqrt{3}l$		"	
-2	$-\frac{1}{3}\sqrt{3}l$			"
-1	$-\frac{1}{12}\sqrt{3}l$			"
0	0	"		
+1	$+\frac{1}{4}\sqrt{3}l$	"		
+2	$+\frac{1}{3}\sqrt{3}l$		"	
+3	$+\frac{7}{12}\sqrt{3}l$		"	
+4	$+\frac{2}{3}\sqrt{3}l$			"
+5	$+\frac{11}{12}\sqrt{3}l$			"
+6	$+\sqrt{3}l$	"		
+7	$+\frac{5}{4}\sqrt{3}l$	"		
+8	$+\frac{4}{3}\sqrt{3}l$		"	

the plane from the zero plane, namely the value of  $z$ , in terms of the elementary cube edge. The last three columns indicate the arrangements of the axes of the atoms as being like either fig. 1 A, the zero plane, fig. 1 B, plane -1, or fig. 1 C, plane +2. Because the lattice is, so to speak, two face-centred lattices together at a distance  $\frac{1}{4}\sqrt{3}l$  apart (the



wider interval in the model) adjacent planes separated by a wide interval are identical, namely plane 0 is like plane +1, +2 like +3, +4 like +5, and so on.

Table XI. gives the radii of 24 concentric spheres in the

TABLE XI.  
Diamond Lattice.

Sphere No. Diamond Lattice.	Radius sphere diamond.	Corresponding Sphere No. Cubic Lattice. Double radius.	Sphere No. Diamond Lattice.	Radius sphere diamond.	Corresponding Sphere No. Cubic Lattice. Double radius.
1	$\frac{1}{4} \sqrt{3} = 0.4330$ <i>l</i>		13	$\frac{1}{4} \sqrt{51} = 1.7854$ <i>l</i>	
2	$\frac{1}{2} \sqrt{2} = 0.7071$ „	2	14	$\frac{1}{2} \sqrt{14} = 1.8709$ „	13
3	$\frac{1}{4} \sqrt{11} = 0.8292$ „		15	$\frac{1}{4} \sqrt{59} = 1.9203$ „	
4	1.0000 „	4	16	2 = 2.0000 „	14
5	$\frac{1}{4} \sqrt{19} = 1.0897$ „		17	$\frac{1}{4} \sqrt{67} = 2.0464$ „	
6	$\frac{1}{2} \sqrt{6} = 1.2248$ „	6	18	$\frac{3}{2} \sqrt{2} = 2.1213$ „	16
7	$\frac{3}{4} \sqrt{5} = 1.2990$ „		19	$\frac{5}{4} \sqrt{3} = 2.1651$ „	
8	$\sqrt{2} = 1.4142$ „	7	20	$\sqrt{5} = 2.2361$ „	18
9	$\frac{1}{4} \sqrt{35} = 1.4790$ „		21	$\frac{1}{4} \sqrt{83} = 2.2776$ „	
10	$\frac{1}{2} \sqrt{10} = 1.5812$ „	9	22	$\frac{1}{2} \sqrt{22} = 2.3452$ „	20
11	$\frac{1}{4} \sqrt{43} = 1.6394$ „		23	$\frac{1}{4} \sqrt{91} = 2.3849$ „	
12	$\sqrt{3} = 1.7321$ „	11	24	$\sqrt{6} = 2.4495$ „	21

diamond lattice including 488 atoms. The last column gives the number of the sphere in the simple cubic lattice of Table IV. which is identical in all respects with the sphere of the diamond, provided only the linear dimensions of the simple cubic sphere are each divided by 2, as above

explained. Table XII. gives a more complete specification of the diamond lattice including 24 spheres, plane by plane

TABLE XII.  
Diamond Lattice.

No. Sphere.	Radius Sphere.	No. Plane.	No. Circle.	Cos $\alpha$ .	No. Atoms, Circle.	No. Atoms, Sphere.	Total Atoms.	$\Sigma(-3Zz + \cos \alpha)p^{-3}$ .
1	$\frac{1}{4}\sqrt{3}$ /	-1	1	$-\frac{1}{2}$	3	4	4	-65.6896
	" "	+1	0	$\frac{1}{2}$	1			
2	$\frac{1}{2}\sqrt{2}$ ..	0	1	$-\frac{1}{2}$	6	12	16	-88.3170
	" "	+2	1	"	3			
3	$\frac{1}{4}\sqrt{11}$ ..	3	1	"	3	12	28	-75.5589
	" "	-1	2	$\frac{1}{2}$	3			
	" "	+1	1	$-\frac{1}{2}$	6			
4	/	+2	2	1	3	6	34	"
5	$\frac{1}{4}\sqrt{19}$ ..	-3	2	$\frac{1}{2}$	3	12	46	-77.5112
	" "	-1	3	$-\frac{1}{2}$	6			
	" "	+3	1	"	3			
6	$\frac{1}{2}\sqrt{6}$ ..	0	2	"	6	24	70	-68.8018
	" "	+2	3	"	6			
	" "	+4	1	"	3			
7	$\frac{3}{4}\sqrt{3}$ ..	-5	0	$\frac{1}{2}$	1	16	86	-73.7084
	" "	-3	3	$-\frac{1}{2}$	6			
	" "	+1	2	"	6			
	" "	+3	2	$\frac{1}{2}$	3			
8	$\sqrt{2}$ ..	0	3	1	6	12	98	"
	" "	+4	2	$\frac{1}{2}$	3			
9	$\frac{1}{4}\sqrt{35}$ ..	-5	1	$-\frac{1}{2}$	6	24	122	-69.4165
	" "	-1	4	"	6			
	" "	+1	3	$\frac{1}{2}$	6			
	" "	+3	3	$-\frac{1}{2}$	6			

5. Table VI. follows immediately from the correspondences in Table V. The numbers of the planes set opposite to each other in Table VI. are those in which the atoms are located in an identical manner including the directions of their axes.

TABLE VI.

No. plane.	Face-centred Lattice.	Simple Cubic Lattice.
	8	16
	7	14
	6	12
	5	10
	4	8
	3	6
	2	4
	1	2
	0	0

6. It follows from Table VI. that a face-centred lattice may be formed from a simple cubic lattice merely by omitting all of the odd planes of the cubic lattice, and then reducing the dimensions of the lattice by a factor of 2, because the edge of the equilateral triangle of the cubic is twice that of the face-centred lattice. Consequently the same computations made above for the simple cubic may now be used for the face-centred lattice, provided we substitute  $\frac{1}{2}l$  for  $l$ . In the  $r^{-3}$  term of the force-equation this makes  $l^{-3}$  eight times its former value.

7. By consulting Tables III. and IV. for the simple cubic lattice it will appear that when all of the odd planes are omitted the numbers of the concentric spheres that remain are given by the upper row of figures in Table VII. These spheres alone therefore constitute a face-centred lattice, some spheres having even and some odd numbers. The spheres may then be renumbered consecutively as in the lower row of figures. Sphere No. 16, for example, of the face-centred lattice is identical in all respects with sphere No. 18 of the simple cubic lattice when its dimensions are divided by 2.

TABLE VII.

## Numbers of Spheres.

Cubic .....	2, 4, 6, 7, 9, 11, 13, 14, 16, 18, 20, 21, 23, 26, 27, 29.
Face-centred ...	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16

8. It is no longer true, however, that each sphere of the face-centred lattice embraces atoms either in odd or even planes, as was the case with the cubic lattice. This is because some of the even planes of the cubic receive an odd number in the face-centred lattice. The numbers of the spheres of the face-centred lattice that contain atoms in even, odd, or even and odd planes is given in Table VIII.

TABLE VIII.

	Even planes.	Odd planes.	Even and Odd planes.	
Sphere numbers,	4	1	3	11
Face-centred	8	2	5	13
Cubic Lattice.	12	6	7	14
	15	10	9	16

9. It still holds true, however, that  $\cos \alpha$  has the same value for each atom in any one sphere, being either  $-1/3$  or  $+1$ .

10. The face-centred lattice is also symmetrical about the centre, that is to say about any selected atom. Each atom is matched by another at the same distance on the opposite side of the centre, having its axis parallel to that of the given atom. The direction cosines  $X$ ,  $Y$ , and  $Z$  are each reversed in sign for the second atom of such a pair.

11. It follows from the statement in 10 that the sum of the  $r^{-4}$  terms of the force equation (9) will vanish for the face-centred lattice as they did for the cubic lattice, because the direction cosines occur in odd degrees only.

12. The sum of the forces according to (2) or (9) may, therefore, be found for the whole face-centred lattice by the use of Table IV. compiled for the simple cubic lattice by picking out those spheres only that form the face-centred lattice according to Table VII., and multiplying each sum by 8 for the reason above stated. This result is given in Table IX. The numbers given are, however, the same as for the cubic lattice in Table IV., the final result only being multiplied by 8 instead of the individual sums for each sphere.

For a face-centred cubic lattice, therefore, comprising 16 spheres embracing 428 atoms, we find

$$S = \Sigma(-3Z\xi + \cos \alpha)p^{-3} = -17.659. \quad \dots (16)$$

And according to (2) or (9) the whole force upon the positive charge of the single hydrogen atom at the centre is

$$F_z = \frac{e^2}{k}(-35.32)Dl^{-3}. \quad \dots (17)$$

TABLE IX.  
Face-centred Cubic Lattice.

No. Sphere.	Radius sphere.	$\cos \alpha$ .	Atoms in sphere.	Atoms, total.	$\frac{1}{8}\Sigma(-3Z\zeta + \cos \alpha)p^{-3}$ .		
					For sphere.		Total for face-centred cubic lattice.
					+	-	
1	$\frac{1}{2}\sqrt{2}$ "	$-\frac{1}{3}$	12	12		2.82842	-2.82842
2	1 "	1	6	18	0		"
3	$\frac{1}{2}\sqrt{6}$ "	$-\frac{1}{3}$	24	42	1.08866		-1.30976
4	$\sqrt{2}$ "	1	12	54	0		"
5	$\frac{1}{2}\sqrt{10}$ "	$-\frac{1}{3}$	24	78		0.50597	-2.24573
6	$\sqrt{3}$ "	1	8	86	0		"
7	$\frac{1}{2}\sqrt{14}$ "	$-\frac{1}{3}$	48	134		0.087070	-2.33300
8	2 "	1	6	140	0		"
9	$\frac{3}{2}\sqrt{2}$ "	$-\frac{1}{3}$	36	176	0.244431		-2.08857
10	$\sqrt{5}$ "	1	24	200	0		"
11	$\frac{1}{2}\sqrt{22}$ "	$-\frac{1}{3}$	24	224		0.070479	-2.15905
12	$\sqrt{6}$ "	1	24	248	0		"
13	$\frac{1}{2}\sqrt{26}$ "	$-\frac{1}{3}$	72	320	0.083552		-2.07550
14	$\frac{1}{2}\sqrt{30}$ "	$-\frac{1}{3}$	48	368		0.084389	-2.15989
15	$2\sqrt{2}$ "	1	12	380	0		"
16	$\frac{1}{2}\sqrt{34}$ "	$-\frac{1}{3}$	48	428		0.047474	-2.20736
$\Sigma(-3Z\zeta + \cos \alpha)p^{-3} = -17.659.$							

Comparing this result with (8) for the simple cubic lattice it appears that the sign has changed and that the value is more than four times larger. As pointed out above, it is necessary that the sign be negative to satisfy the requirements. The simple cubic lattice would not answer for a single element because of the sign being wrong. As

before, we may now equate this new expression in (17) to (12) and find

$$-35.32 D l^{-3} = -30.7 \times 10^{24} D, \quad . \quad . \quad . \quad (18)$$

from which  $D$  cancels giving

$$l^{-3} = 0.87 \times 10^{24}; \quad l = 1.05 \times 10^{-8} \text{ cm.} \quad . \quad . \quad (19)$$

This result admits of the possibility that hydrogen may form face-centred cubic crystals, but it is by no means conclusive. The test has now advanced one step further than before without meeting with any obstacle. We might now turn to the experimental evidence contained in the density of solid hydrogen to see whether such a small value of the cube edge as found in (19) can possibly satisfy this density, but it seems a better plan to examine the second theoretical requirement to ascertain whether it too is satisfied.

*The Second Condition to be Satisfied by the Lattice.*

A second theoretical requirement that must be satisfied by any form of lattice is that the total force upon each and every atom in it shall be equal to zero in the condition of stable equilibrium. This involves a second equation which may next be given, the derivation of it being reserved for another paper. The total force of a second hydrogen atom in the position  $X, Y, Z, r$ , and  $\alpha$  upon a first hydrogen atom at the origin with axis along the  $zk$ -axis is as follows:—

$$\begin{aligned} F_z = \frac{3e^2}{k} \{ & f_3 D^2 r^{-4} \\ & + [f_4 b^2 D - \frac{1}{2}(f_5 + f_6) \rho a^2 D] r^{-5} \\ & + [5f_7 b^4 + \frac{5}{2}(f_8 + 2f_9) \rho a^2 b^2 - \frac{5}{2} f_{10} \rho^2 a^4] r^{-6} \}, \quad (20) \end{aligned}$$

where  $f_3$  to  $f_{10}$  are functions of  $X, Y, Z$ , and  $\alpha$  as follows:—

$$f_3 = 5Z^2 \xi - 3Z \cos \alpha + X \sin \alpha, \quad . \quad . \quad . \quad (21)$$

$$\begin{aligned} f_4 = & \cos \alpha (1 - \cos \alpha) (3 - 30Z^2 + 35Z^4) \\ & + 10 \sin \alpha (\frac{1}{2} - \cos \alpha) XZ (3 - 7Z^2) \\ & + \sin^2 \alpha [5(X^2 + Z^2) - 35X^2 Z^2 - 1], \quad . \quad (22) \end{aligned}$$

$$\begin{aligned} f_5 = & 5XZ (3 - 7Z^2) \sin \alpha \\ & + (3 - 30Z^2 + 35Z^4) \cos \alpha, \quad . \quad . \quad . \quad (23) \end{aligned}$$

$$\begin{aligned} f_6 = & 2 - 10Z^2 - 5Y^2 + 35Z^2 (\xi^2 + Y^2) \\ & - 10Z \xi \sin \alpha - 20XZ \sin \alpha \cos \alpha \\ & + (2 - 15Z^2) \sin^2 \alpha - 5X^2 \cos^2 \alpha, \quad . \quad . \quad (24) \end{aligned}$$

$$\begin{aligned}
 * f_7 = & -63Z^3\zeta^2 + Z(21X^2 - 7Z^2 - 3) \sin^2 \alpha \\
 & + Z(70Z^2 - 15) \cos^2 \alpha \\
 & + X(6 - 84Z^2) \sin \alpha \cos \alpha, \quad . \quad . \quad (25)
 \end{aligned}$$

$$\begin{aligned}
 f_8 = & -21Z\zeta^2(1 - 3Z^2) + Z(3 - 7Z^2) \\
 & + 6\zeta(1 - 7Z^2) \cos \alpha + 6Z \cos^2 \alpha, \quad . \quad . \quad (26)
 \end{aligned}$$

$$\begin{aligned}
 f_9 = & -(3 - 7Z^2)(Z + \xi \sin \alpha) \\
 & + 7Z(3Z^2 \sin^2 \alpha + 4XZ \sin \alpha \cos \alpha + X^2 \cos^2 \alpha) \\
 & + \frac{7}{2}Z(1 - 9Z^2)(\xi^2 + Y^2), \quad . \quad . \quad . \quad (27)
 \end{aligned}$$

$$\begin{aligned}
 f_{10} = & 3Z - 7Z(X^2 + 4Y^2 + \xi^2) + \frac{63}{2}Z(\xi^2 + Y^2)(X^2 + Y^2) \\
 & + 2\xi \sin \alpha [1 - \frac{7}{2}(X^2 + Y^2)] \\
 & + (Z \cos \alpha + 2X \sin \alpha - 14XZ\xi) \cos \alpha, \quad (28)
 \end{aligned}$$

where  $\xi = Z \sin \theta + X \cos \alpha$ .

The equation which is equivalent to (20) when the axes of the two hydrogen atoms are parallel to each other has already been published as (100) in the preceding paper †, and it will be found that this reduces to that when we put  $\sin \alpha = 0$ . The equatorial displacement,  $l$ , must also be put equal to zero in that equation in making the comparison, because it is assumed to be zero in (20) above. The equation is there quite fully discussed, and most of the essential points apply also to this more general expression. The striking characteristic is that the series begins with the  $r^{-4}$  term and need not include terms beyond the  $r^{-6}$  term. The  $r^{-4}$  term contains  $D^2$  as a factor, the  $r^{-5}$  contains  $D$ , while the  $r^{-6}$  term contains the fourth degree of  $a$  and  $b$ ,  $a$  being the radius of the circle in the circle-and-point electron and  $b$  its semi-minor axis. If we make  $D=0$ , the  $r^{-4}$  and  $r^{-5}$  terms vanish and no equilibrium would be possible. It requires the presence of these three terms to fulfil the conditions of an equilibrium.

Let us now consider a single pair of atoms of either the cubic or face-centred lattices at equal distances on opposite sides of the selected atom and having axes parallel to each other. Equal values of  $f_3$  in (21) but with opposite signs are obtained for this pair of atoms because  $X$  and  $Z$  occur in each term in an odd degree. Hence the sum of these functions for the pair of atoms is zero. It is, therefore, zero for the whole lattice, and the  $r^{-4}$  term drops out from the equation. The  $r^{-5}$  term does not vanish, but the  $r^{-6}$

\* Since the paper went to press it has been proved that  $f_7 = -f_9 = -2f_{10}$ .  
A. C. Crehore, Phil. Mag. May 1925, p. 868.

term vanishes for a similar reason to that given for the  $r^{-4}$  term, because X, Y, and Z occur in odd degrees in each term of the functions  $f_7, f_8, f_9$ , and  $f_{10}$ .

This furnishes conclusive proof that the sum of the forces (20) written for each atom in the lattice cannot be set equal to zero, for the coefficient of the  $r^{-5}$  term does not vanish, and no adjustment of the size of the cube edge is possible that will make the whole force vanish and produce a stable condition of equilibrium.

The above reasoning rules out any form of lattice for hydrogen that is symmetrical with respect to a centre. This generalization extends the proof so as to exclude the third form of lattice above enumerated, the body-centred cubic lattice, which has not been given in detail. It is thus easier to say what the form of the crystal of solid hydrogen is not than to construct what it is, but even so, results such as these have a practical value that is far from negative. It seems best at this stage to give some consideration to the carbon atom before resuming the discussion of hydrogen.

#### *Carbon.*

The model of the carbon atom that we shall use for purposes of computation was first published in the *Philosophical Magazine* for May 1922, shown in fig. 1, p. 887, and described on p. 890. Some changes\* have been made in some of the other atoms shown at that time in this figure but not in that of carbon, which is shown here in fig. 3 in two views—an axial and an equatorial view.

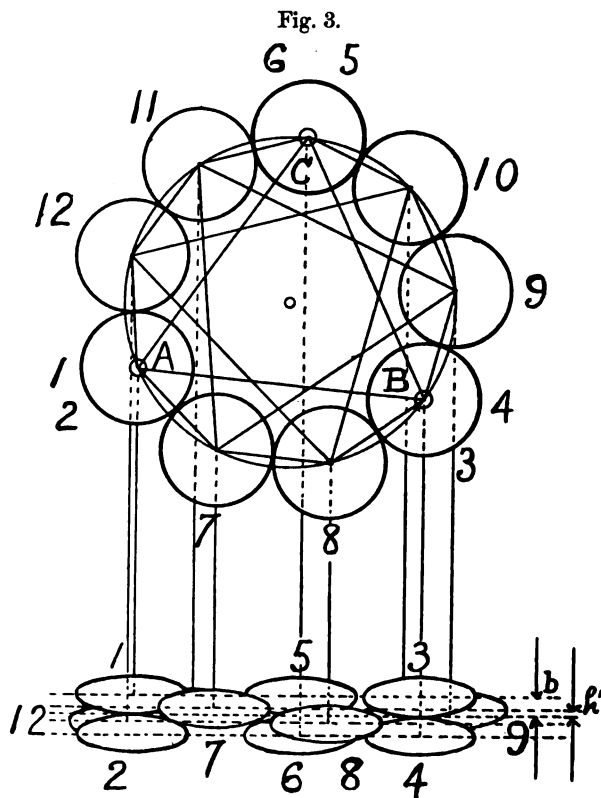
One of the reasons for choosing carbon for investigation here is that there are no isotopes known for carbon, and this is certainly not true for lithium and probably not for glucinum and boron, the next atoms in order of atomic number, excepting helium that forms no compounds. Another reason is the perfect symmetry of the model of the atom, the fact that it has the form of a ring containing three alpha-particles and no hydrogen atoms, and that there exist at least two crystals, the diamond and graphite, with which theoretical results may be compared and checked. And, again, carbon forms many compounds with hydrogen, which may ultimately be worked out in some detail when there has been a satisfactory confirmation of the theory by the use of crystals.

The three positive charges, A, B, and C of fig. 3, in the three alpha-particles of the carbon atom form a perfect equilateral

\* See fig. 2, p. 37, 'The Progress of Atomic Theory,' A. C. Crehore.



triangle in the equatorial plane of the atom. There are then twelve negative electrons, six of them, 1-6, belonging to the alpha-particles, and six, 7-12, serving as the so-called connecting electrons to bind the structure together. There are thus four perfect equilateral triangles of negative electrons,



Detail drawing of the Carbon atom in plan and elevation, showing the distances  $b$  and  $h$ .

the upper ones, 1, 3, and 5, in the alpha-particles forming the first, the lower ones, 2, 4, and 6, the second, the upper three connecting electrons, 7, 9, and 11, the third, and the lower three, 8, 10, and 12, the fourth triangle. The connecting electrons are supposed to be staggered alternately up and down all around the ring; that is to say, they are not exactly in the equatorial plane, but located at about half the distance

from it that the electrons in the alpha-particles have. The reason for this separation from the equator is the mutual repulsion of the adjacent negative connecting electrons. This repulsion is balanced, however, by the strong attraction they have for the alpha-particles, each having an effective charge of  $+2e$ .

In the free carbon atom the common distance of all electrons in the alpha particles from the equator is the same, equal to  $b$ , the semi-minor axis of the negative electron very approximately. Similarly the connecting electrons have the same distance from the equator, the one as the other, say equal to  $h'$ , which differs from  $b$  and is thought to be about half the value of  $b$ . When the atom forms part of a molecule, however, instead of being free, the upper distances,  $b$  and  $h'$ , change to  $b_2$  and  $h_2'$ , and the lower distances are  $-b_1$  and  $-h_1'$ , each of which differs by a very small amount from  $b$  and  $h'$ . The differences,  $D=b_2-b_1$  and  $H=h_2'-h_1'$ , which are zero in a free atom, become appreciable when a molecule is formed. A finite value for  $D$  is in fact demanded in order that a molecule may be formed.

The expression for the force that has been derived from the electrostatic forces for a second such carbon atom acting upon the positive charge only of the first carbon atom at the origin of coordinates, the axis of the latter coinciding with the  $z$ -axis, is as follows:—

$$F_z = \frac{e^2}{k} \left\{ 36f_1(D+H)r^{-3} + 108f_2[(b^2+h'^2)-\rho a^2]r^{-4} \dots \right\}, \quad (29)$$

$\begin{matrix} \text{C}_2 \text{ on} \\ 3 \text{ positive charges} \\ \text{of first atom.} \end{matrix}$

where the functions,  $f_1$  and  $f_2$ , are identical with those determined in the case of hydrogen given above by (10) and (11). The corresponding expression for hydrogen was given in (9). If in (29) we should make  $h'=b$  and  $H=D$ , then it is seen that the force becomes exactly 36 times that of (9), 36 being the square of the atomic number of carbon. But  $h'$  is not equal to  $b$ , nor  $H$  to  $D$  in the carbon atom, and it is here that the character of the expression for carbon differs from that for hydrogen. Otherwise we might form the same conclusions from this equation that were drawn from (9) for hydrogen.

Without making any use of (29) for the moment, let us pass immediately to the second condition which must be satisfied by any form of lattice structure. For this we require the force of a second carbon atom upon the whole

of the first atom at the origin. This has been proven to be as follows:—

$$F_z = \frac{e^2}{k} \left\{ 27f_3(D+H)^2r^{-4} \right. \\ \text{Second carbon atom} \quad + 27[f_4(b^2+h'^2) - f_5\rho a^2 - f_6\rho a^2](D+H)r^{-5} \\ \text{on first carbon atom.} \quad + 135[f_7(b^2+h'^2)^2 + (f_8+2f_9)\rho a^2(b^2+h'^2) \\ \left. - 2f_{10}\rho^2a^4\right]r^{-6} \dots \}, \quad (30)$$

where the functions  $f_3$  to  $f_{10}$  are given by (21) to (28), being identical with those obtained in the case of hydrogen.

Here also it is seen that, if  $h'=b$  and  $H=D$ , equation (30) is exactly 36 times (20), the corresponding expression for hydrogen. But this is not true, a fact which gives rise to some differences between the two equations. However, because the functions  $f_3$  to  $f_{10}$  are the same as before, we find that, when the forces of a single pair of atoms on opposite sides of the selected atom at the same distance and having parallel axes are added together, both the  $r^{-4}$  and the  $r^{-6}$  terms of (30) vanish, leaving only the  $r^{-5}$  term. As pointed out above, this proves conclusively that no form of lattice having a centre of symmetry can satisfy the condition that the sum of the forces for the lattice shall be zero. From this it follows that carbon will neither crystallize in the form of a simple cubic lattice, a face-centred cubic, nor a body-centred cubic lattice. This conclusion is undoubtedly true, the structure of both the diamond and graphite being different from the lattices named.

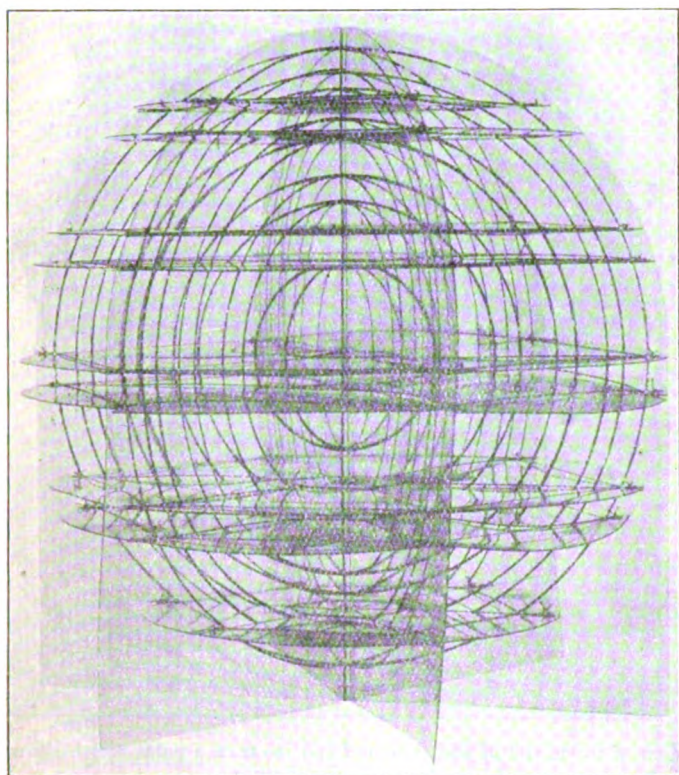
There is a double reason why the simple cubic lattice will not answer, namely that neither the first nor the second condition is satisfied, the first condition involving the sum of equations like (29) for the lattice, and the second like (30). The sum of (29) comes out positive for the cubic lattice, whereas it must be negative as pointed out. The sum of (30) must be zero, and this condition cannot be satisfied. On the other hand, the face-centred cubic lattice satisfies the first condition, since the sum of (29) is negative as shown. The sum of (30), however, cannot be zero.

Now it is well known that there are a number of elements which crystallize as a face-centred lattice. It may be presumed, therefore, that the fundamental equation for such elements corresponding to (30) will contain in the  $r^{-4}$  and  $r^{-6}$  terms functions of  $X$ ,  $Y$ , and  $Z$  including a constant term that does not change sign by a reversal of their signs. Aluminium is an example of an element that forms a face-centred lattice, and aluminium happens to be the atom of highest atomic number for which a model has been

constructed. It can already be seen from its model that such terms as referred to make their appearance in the case of aluminium, and we may expect that this second condition that is not satisfied by carbon will be fulfilled by aluminium, thus allowing the formation of the face-centred lattice. But the case of aluminium is not completed, and no more can be stated here than that it seems probable that it will yield a face-centred lattice.

*The Diamond Lattice.*

Fig. 4 A.

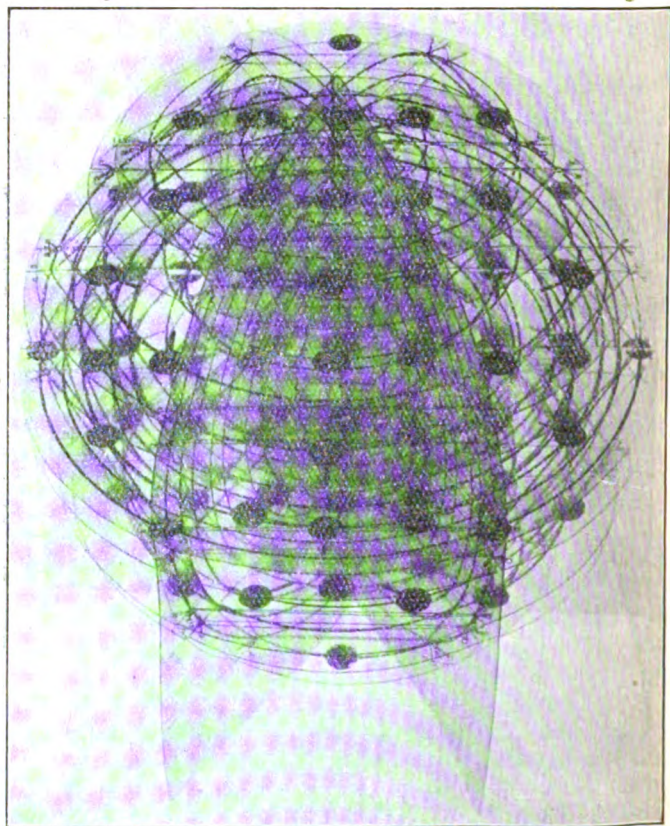


Side view of the model of the Diamond Lattice, showing eight concentric spheres of atoms.

A model of the diamond lattice constructed along the same lines as that of the simple cubic lattice above described and shown in figs. 2 A and 2 B is pictured in figs. 4 A

and 4 B in two different views. This lattice consists of two interpenetrating face-centred cubic lattices displaced along the direction of the diagonal of the cube by a distance from each other of  $\frac{3}{4}$  the altitude of the regular tetrahedron, whose base is one of the elementary equilateral

Fig. 4 B.



View of the model of the Diamond Lattice from a point which shows the cubical structure.

triangles. There are nine of the (111) planes shown in the model, which include 98 atoms in 8 concentric spheres surrounding the selected atom. A scheme for this lattice is shown in Table X. The first column gives the number of the (111) plane, and the second column the distance of

TABLE X.  
Diamond Lattice.

No. Plane.	$z$ of plane.	Like Fig. 1 A.	Like Fig. 1 C.	Like Fig. 1 B.
-8	$-\frac{4}{3}\sqrt{3} l$			"
-7	$-\frac{13}{12}\sqrt{3} "$			"
-6	$-\sqrt{3} "$	"		
-5	$-\frac{3}{4}\sqrt{3} "$	"		
-4	$-\frac{2}{3}\sqrt{3} "$		"	
-3	$-\frac{5}{12}\sqrt{3} "$		"	
-2	$-\frac{1}{3}\sqrt{3} "$			"
-1	$-\frac{1}{12}\sqrt{3} "$			"
0	0	"		
+1	$+\frac{1}{4}\sqrt{3} "$	"		
+2	$+\frac{1}{3}\sqrt{3} "$		"	
+3	$+\frac{7}{12}\sqrt{3} "$		"	
+4	$+\frac{2}{3}\sqrt{3} "$			"
+5	$+\frac{11}{12}\sqrt{3} "$			"
+6	$+\sqrt{3} "$	"		
+7	$+\frac{5}{4}\sqrt{3} "$	"		
+8	$+\frac{4}{3}\sqrt{3} "$		"	

the plane from the zero plane, namely the value of  $z$ , in terms of the elementary cube edge. The last three columns indicate the arrangements of the axes of the atoms as being like either fig. 1 A, the zero plane, fig. 1 B, plane -1, or fig. 1 C, plane +2. Because the lattice is, so to speak, two face-centred lattices together at a distance  $\frac{1}{4}\sqrt{3} l$  apart (the

wider interval in the model) adjacent planes separated by a wide interval are identical, namely plane 0 is like plane +1, +2 like +3, +4 like +5, and so on.

Table XI. gives the radii of 24 concentric spheres in the

TABLE XI.  
Diamond Lattice.

Sphere No. Diamond Lattice.	Radius sphere diamond.	Corresponding Sphere No. Cubic Lattice. Double radius.	Sphere No. Diamond Lattice.	Radius sphere diamond.	Corresponding Sphere No. Cubic Lattice. Double radius.
1	$\frac{1}{4} \sqrt{3} = 0.4330$ <i>l</i>		13	$\frac{1}{4} \sqrt{51} = 1.7854$ <i>l</i>	
2	$\frac{1}{2} \sqrt{2} = 0.7071$ ..	2	14	$\frac{1}{2} \sqrt{14} = 1.8709$ ..	13
3	$\frac{1}{4} \sqrt{11} = 0.8292$ ..		15	$\frac{1}{4} \sqrt{59} = 1.9203$ ..	
4	1.0000 ..	4	16	2 = 2.0000 ..	14
5	$\frac{1}{4} \sqrt{19} = 1.0897$ ..		17	$\frac{1}{4} \sqrt{67} = 2.0464$ ..	
6	$\frac{1}{2} \sqrt{6} = 1.2248$ ..	6	18	$\frac{3}{2} \sqrt{2} = 2.1213$ ..	16
7	$\frac{3}{4} \sqrt{3} = 1.2990$ ..		19	$\frac{5}{4} \sqrt{3} = 2.1651$ ..	
8	$\sqrt{2} = 1.4142$ ..	7	20	$\sqrt{5} = 2.2361$ ..	18
9	$\frac{1}{4} \sqrt{35} = 1.4790$ ..		21	$\frac{1}{4} \sqrt{83} = 2.2776$ ..	
10	$\frac{1}{2} \sqrt{10} = 1.5812$ ..	9	22	$\frac{1}{2} \sqrt{22} = 2.3452$ ..	20
11	$\frac{1}{4} \sqrt{43} = 1.6394$ ..		23	$\frac{1}{4} \sqrt{91} = 2.3849$ ..	
12	$\sqrt{3} = 1.7321$ ..	11	24	$\sqrt{6} = 2.4495$ ..	21

diamond lattice including 488 atoms. The last column gives the number of the sphere in the simple cubic lattice of Table IV. which is identical in all respects with the sphere of the diamond, provided only the linear dimensions of the simple cubic sphere are each divided by 2, as above



explained. Table XII. gives a more complete specification of the diamond lattice including 24 spheres, plane by plane

TABLE XII.  
Diamond Lattice.

No. Sphere.	Radius Sphere.	No. Plane.	No. Circle.	Cos $\alpha$ .	No. Atoms, Circle.	No. Atoms, Sphere.	Total Atoms.	$\Sigma(-3Z' + \cos \alpha)p^{-3}$ .
1	$\frac{1}{4}\sqrt{3}$ /	-1	1	$-\frac{1}{3}$	3			
"	" "	+1	0	$\frac{1}{3}$	1	4	4	-65.6896
2	$\frac{1}{2}\sqrt{2}$ ..	0	1	$-\frac{1}{3}$	6			
"	" "	+2	1	"	3	12	16	-88.3170
3	$\frac{1}{4}\sqrt{11}$ ..	-3	1	"	3			
"	" "	-1	2	$\frac{1}{3}$	3			
"	" "	+1	1	$-\frac{1}{3}$	6	12	28	-75.5589
4	/	+2	2	1	3	6	34	..
5	$\frac{1}{4}\sqrt{19}$ ..	-3	2	1	3			
"	" "	-1	3	$-\frac{1}{3}$	6			
"	" "	+3	1	"	3	12	46	-77.5112
6	$\frac{1}{2}\sqrt{6}$ ..	0	2	"	6			
"	" "	+2	3	"	6			
"	" "	+4	1	"	3	24	70	-68.8018
7	$\frac{3}{4}\sqrt{3}$ ..	-5	0	1	1			
"	" "	-3	3	$-\frac{1}{3}$	6			
"	" "	+1	2	"	6			
"	" "	+3	2	1	3	16	86	-73.7084
8	$\sqrt{2}$ ..	0	3	1	6			
"	" "	+4	2	1	3	12	98	..
9	$\frac{1}{4}\sqrt{35}$ ..	-5	1	$-\frac{1}{3}$	6			
"	" "	-1	4	"	6			
"	" "	+1	3	1	6			
"	" "	+3	3	$-\frac{1}{3}$	6	24	122	-69.4165



TABLE XII. (continued).

No. Sphere.	Radius Sphere.	No. Plane.	No. Circle.	Cos $\alpha$ .	No. Atoms, Circle.	No. Atoms, Sphere.	Total Atoms.	$\Sigma(-3Z\zeta + \cos \alpha)p^{-3}$ .
10	$\frac{1}{2}\sqrt{10}$ l	+2	4	$-\frac{1}{3}$	6			
"	" "	+4	3	"	6	24	146	-73.4643
11	$\frac{1}{4}\sqrt{43}$ "	-3	4	"	6			
"	" "	-1	5	$\frac{1}{3}$	3			
"	" "	+5	1	$-\frac{1}{3}$	3	12	158	-71.6907
12	$\sqrt{3}$ "	+2	5	1	3			
"	" "	+6	0	1	1	8	166	"
13	$\frac{1}{4}\sqrt{51}$ "	-5	2	$-\frac{1}{3}$	6			
"	" "	-3	5	$\frac{1}{3}$	3			
"	" "	-1	6	$-\frac{1}{3}$	6			
"	" "	+3	4	"	6			
"	" "	+5	2	1	3	24	190	-72.9035
14	$\frac{1}{2}\sqrt{14}$ "	0	4	$-\frac{1}{3}$	12			
"	" "	+2	6	"	6			
"	" "	+4	4	"	6			
"	" "	+6	1	"	6	48	238	-73.6017
15	$\frac{1}{4}\sqrt{59}$ "	-7	1	"	3			
"	" "	-5	3	$\frac{1}{3}$	6			
"	" "	-3	6	$-\frac{1}{3}$	6			
"	" "	+1	4	"	12			
"	" "	+3	5	$\frac{1}{3}$	3			
"	" "	+5	3	$-\frac{1}{3}$	6	36	274	-74.2527
16	2 "	+4	5	1	3	6	280	"
17	$\frac{1}{4}\sqrt{67}$ "	-7	2	$\frac{1}{3}$	3			
"	" "	-1	7	$-\frac{1}{3}$	3			
"	" "	+3	6	"	6	12	292	-75.6740

TABLE XII. (continued).

No. Sphere.	Radius Sphere.	No. Plane.	No. Circle.	Cos $\alpha$ .	No. Atoms, Circle.	No. Atoms, Sphere.	Total Atoms.	$\Sigma(-3Z'_s + \cos \alpha)p^{+3}$ .
18	$\frac{3}{2}\sqrt{2} \ l$	0	5	$-\frac{1}{3}$	6			
"	" "	+2	7	"	3			
"	" "	+4	6	"	6			
"	" "	+6	2	"	6	36	328	-73·7186
19	$\frac{5}{4}\sqrt{3} \ ,$	-7	3	"	6			
"	" "	-3	7	"	3			
"	" "	-1	8	1	6			
"	" "	+1	5	$-\frac{1}{3}$	6			
"	" "	+5	4	"	6			
"	" "	+7	0	1	1	28	356	-72·6886
20	$\sqrt{5} \ ,$	+2	8	1	6			
"	" "	+6	3	1	6	24	380	"
21	$\frac{1}{4}\sqrt{83} \ ,$	-5	4	$-\frac{1}{3}$	12			
"	" "	-3	8	1	6			
"	" "	-1	9	$-\frac{1}{3}$	6			
"	" "	+3	7	"	3			
"	" "	+5	5	1	3			
"	" "	+7	1	$-\frac{1}{3}$	6	36	416	-72·1216
22	$\frac{1}{2}\sqrt{22} \ ,$	+2	9	"	6			
"	" "	+4	7	"	3			
"	" "	+8	1	"	3	24	440	-72·6855
23	$\frac{1}{4}\sqrt{91} \ ,$	-7	4	"	6			
"	" "	-3	9	"	6			
"	" "	+3	8	1	6			
"	" "	+5	6	$-\frac{1}{3}$	6	24	464	-72·1410
24	$\sqrt{6} \ ,$	0	6	1	6			
"	" "	+4	8	1	6			
"	" "	+8	2	1	3	24	488	"

and circle by circle in these planes. The last column gives the important total summation of  $f_1$  of equation (10) when multiplied by  $p^{-3}$ , where  $p=r/l$ , for all the spheres from the first to the given sphere inclusive. By this last column it is seen that the first sphere gives the largest sum, but that for a very accurate value for an infinite lattice probably more than 24 spheres should be computed.

Table XIII. gives the sum of  $p^{-4}f_2$ , where  $f_2$  is given by (11) above. This Table includes but 6 spheres and 70 atoms. The more rapid decrease in this sum per sphere with increasing sphere number is due to the higher order of the term,  $r^{-4}$  instead of  $r^{-3}$  above, so that an approximate value for an infinite lattice is obtained from 6 spheres.

TABLE XIII.  
Diamond Lattice.

No. sphere.	No. atoms.	$\Sigma p^{-4}f_2$ sphere.	$\Sigma p^{-4}f_2$ total.
1	4	-44.949	-44.949
2	12	0	-44.949
3	12	-10.952	-55.901
4	6	0	-55.901
5	12	+0.3515	55.55
6	24	0	-55.55
Total..... 70			

By the use of the sums in Tables XII. and XIII. it is possible to write down the sum of equation (29) for the whole diamond lattice. The total force upon the positive charge of the selected carbon atom at the origin due to the whole surrounding lattice of carbon atoms is, therefore, approximately

$$F_r = \frac{e^2}{k} \{ 36(-72.14)(D+H)l^{-3} + 108(-55.55)[(b^2+h'^2) - \rho a^2]l^{-4} \dots \}. \quad (31)$$

Diamond lattice on 3 + charges.

The force upon just one positive charge of one of the

alpha-particles of one carbon atom is, therefore, one third of the above force, and this may be equated to the expression in (12) above because the same reasoning applies here as there, the value of  $\rho_z$  having been derived from the properties of the electron itself. Hence we find the equation representing the first condition that must be satisfied by the carbon lattice, namely

$$\begin{aligned} -865\cdot68(D+H)l^{-3} - 1999\cdot8[(b^2 + h^2) - \rho a^2]l^{-4} \\ = -30\cdot7 \times 10^{24}D. \quad (32) \end{aligned}$$

The second condition is that the sum of the forces of all atoms in the lattice upon the whole of each and every atom in the lattice shall be equal to zero. If the lattice were constructed of hydrogen atoms the sum of the forces given by (20) above must be zero, but if constructed of carbon atoms the sum of the forces given by (30) must vanish. Since both these equations involve the same functions of  $X$ ,  $Y$ , and  $Z$ , it seems best to consider them together in order that their differences may be emphasized. The sums of the functions  $f_3$  to  $f_{10}$  given in (21) to (28) are found for the diamond lattice to be as follows:—Since  $f_3$  is the coefficient of an  $r^{-4}$  term, it has been summed for six concentric spheres including 70 atoms, but  $f_4$ ,  $f_5$ , and  $f_6$  have been summed for only three spheres, 28 atoms, these being coefficients of an  $r^{-5}$  term; while  $f_7$  to  $f_{10}$  have been summed for but two spheres, 16 atoms. We find for the diamond form of lattice

$$\Sigma f_3 r^{-4} = 89\cdot218 l^{-4}, \quad . \quad . \quad . \quad (33)$$

$$\Sigma f_4 r^{-5} = -1022\cdot597 l^{-5}, \quad . \quad . \quad . \quad (34)$$

$$\Sigma (f_5 + f_6) r^{-5} = -1015\cdot575 l^{-5}, \quad . \quad . \quad . \quad (35)$$

$$\Sigma f_7 r^{-6} = -2217\cdot496 l^{-6}, \quad . \quad . \quad . \quad (36)$$

$$\Sigma (f_8 + 2f_9) r^{-6} = 1917\cdot83 l^{-6}, \quad . \quad . \quad . \quad (37)$$

$$\Sigma f_{10} r^{-6} = 775\cdot374 l^{-6}, \quad . \quad . \quad . \quad (38)$$

Substituting these summations in (20) gives the force of the whole lattice of hydrogen atoms upon the one hydrogen atom as

$$\begin{aligned} F_s = \frac{3e^2}{k} \{ 89\cdot218 D^2 l^{-4} - 1022\cdot597 b^2 D l^{-5} \\ + 507\cdot788 \rho a^2 D l^{-5} - 11087\cdot48 b^4 l^{-6} \\ + 4794\cdot58 \rho a^2 b^2 l^{-6} - 1938\cdot44 \rho^2 a^4 l^{-6} \} = 0. \\ . \quad . \quad . \quad (39) \end{aligned}$$

Diamond form  
of lattice  
on H.

And substituting them in (20) gives the force of the whole lattice of carbon atoms upon one carbon atom as

$$F_z = \frac{27e^2}{k} \left\{ 89 \cdot 218(D+H)^2 l^{-4} - 1022 \cdot 597(b^2 + h'^2)(D+H)l^{-5} \right. \\ \text{Diamond} \quad + 1015 \cdot 58 \rho a^2 (D+H)l^{-5} - 11087 \cdot 48(b^2 + h'^2)l^{-6} \\ \text{lattice} \quad + 9589 \cdot 15 \rho a^2 (b^2 + h'^2)l^{-6} - 7753 \cdot 74 \rho^2 a^4 l^{-6} \} = 0. \\ \text{on C.} \quad \dots (40)$$

Equation (39) proves that the hydrogen atom does not fulfil the necessary conditions to enable it to form a crystal in the form of the diamond lattice, and so this is quickly disposed of. For, after putting in the numerical\* values

$$b^2 = 10^{-26} \quad \text{and} \quad \rho a^2 = 4 \cdot 484 \times 10^{-26}, \dots (41)$$

multiplying each term by  $l^6$  and dividing by the coefficient of  $D^2 l^2$ , we have from (39) the quadratic equation in terms of  $Dl$  as follows:

$$D^2 l^2 + 14 \cdot 05 \times 10^{-26} Dl + 95 \cdot 0 \times 10^{-52} = 0; \dots (42)$$

whence

$$Dl = (-7 \cdot 025 \pm \sqrt{-45 \cdot 65}) 10^{-26}, \dots (43)$$

an imaginary quantity. Both  $D$  and  $l$  must have real values to satisfy the requirements for the lattice, and hence it was rightly concluded above that hydrogen cannot form crystals in a form like that of diamond.

Let us, therefore, turn to the carbon atom lattice in the form of the diamond. The two conditions to be satisfied are (32) and (40). As pointed out before, the force in (40) would be exactly 36 times that in (39) for hydrogen, if we put  $h' = b'$  and  $H = D$ . If this were true we should be obliged to conclude as above for hydrogen that the diamond form of lattice will not satisfy the equation for carbon either. From this it becomes evident that the important thing is the location of the connecting electrons, that is to say, their distance from the equatorial plane of the carbon atom, the quantity  $h'$  in the equations.

Now the value of  $h'$  for a connecting electron is substantially a fixed value, estimated to be about one half of  $b$ , the semi-minor axis of the electron at all times, but it varies to a very minute extent in the different forms of molecule just as  $b$  varies. The value found for  $h'$  should be very closely the same whatever form of molecule is examined, whether diamond, graphite,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and so on; but the

\* Phil. Mag. May 1925, p. 888, eq. (9).

values found for D and H, the small differences between the upper and lower distances should vary considerably from one form to another, since they are connected with the energies of formation and dissociation of the molecule in question. It may be seen from a study of the manner in which the forces act upon the electrons shown by the drawing of the model of the carbon atom in fig. 3 that H will be approximately the same proportion of D that  $h'$  is of  $b$ . Let us assume for a first approximation, which will be slightly modified as we proceed, that this ratio is exactly one half. If so, equations (32) and (40) contain only D and  $l$  as the unknown quantities, since  $b^2$  and  $pa^2$  are known numerically, as given in (41) above. Consequently they may be solved very readily for both the unknown quantities, D and  $l$ , since under this hypothesis (40) reduces to a quadratic in terms of  $l$  similar to (42). The value obtained for the cube edge,  $l$ , however, under the supposition that  $h' = 0.5b$ , does not come out exactly equal to the experimental value of  $l$  for the diamond. This ratio assumed as 0.5 above requires to be slightly altered to approximately

$$h' = 0.42b \quad \text{and} \quad H = 0.42D, \quad . \quad . \quad . \quad (44)$$

when the solution of the two simultaneous equations (32) and (40) gives exactly

$$l = 3.56 \times 10^{-8} \text{ cm.} \quad \text{and} \quad D = -11.9 \times 10^{-18} \text{ cm.,} \quad (45)$$

the former being the experimental value for the cube edge. In fact, when  $l = 3.56 \times 10^{-8} \text{ cm.}$  and  $h'$  and H as in (44) are substituted in (32), we find immediately

$$D = -11.92 \times 10^{-18} \text{ cm.} \quad . \quad . \quad . \quad (46)$$

When they are substituted in (40) we have the quadratic equation

$$D^2 + 7.4296 \times 10^{-18}D = 52.88 \times 10^{-36}, \quad . \quad . \quad (47)$$

from which

$$D = -11.88 \times 10^{-18} \text{ cm.} \quad \text{or} \quad +4.45 \times 10^{-18} \text{ cm.} \quad (48)$$

The negative values of D in (46) and (48) are very closely the same, and a value of  $h'$  very slightly in excess of  $0.42b$  will make the two values of D identical. This value for D incidentally is not far different from that found for the hydrogen molecule in the previous paper\*, namely  $14.47 \times 10^{-18} \text{ cm.}$

Both conditions are, therefore, perfectly satisfied by the

\* Phil. Mag. May 1925, p. 882, eq. (66).

form of the diamond lattice, by its absolute dimensions, and by the model of the carbon atom shown in fig. 3, and we may conclude on theoretical grounds alone that the carbon atom may form such a crystal.

The negative value of  $D$  shows that the force upon the positive charge is positive according to (12), that is in an upward direction away from the base and toward the apex of the regular tetrahedron of atoms forming the first surrounding sphere in the lattice. Hence the electron on the side of this apex is the one that is compressed, while that on the side toward the base is the one that is expanded.

This completes the account of the diamond, and we would naturally turn next to graphite for still further confirmation of these ideas. Graphite, however, does not come under the head of the cubic or isometric system of crystals, and as yet its study has not been completed. There is the problem of determining the directions of the axes of each atom in the crystal before any of the above equations for the carbon atom may be applied. We shall conclude the paper by making some suggestions as to a possible form for a crystal of solid hydrogen.

### *The Hydrogen Lattice.*

It has been shown above that hydrogen will not crystallize in the form of any one of the four lattices of the cubic system considered. The question remains, "how does it crystallize?" The investigation has not proceeded far enough to enable this question to be answered with definiteness, but there are certain indications worth noting. The first of these is the measured density of liquid hydrogen. Dewar gives it as 0.070 at  $-252^{\circ}\text{C.}$ , but the writer has found no record of the density of solid hydrogen. Lacking this, it may be assumed that the density is roughly 0.08, because the ratio of 8/7 is not far from that which the solid to the liquid form has in a number of the elements.

If hydrogen formed a simple cubic lattice, which it does not, this density would give the cube edge as

$$l = 2.75 \times 10^{-8} \text{ cm.}, \quad . \quad . \quad . \quad . \quad (49)$$

but if it formed a face-centred lattice the same density would give

$$l = 4.36 \times 10^{-8} \text{ cm.} \quad . \quad . \quad . \quad . \quad (50)$$

and the distance between nearest atoms would be

$$\frac{1}{2} \sqrt{2}l = 3.08 \times 10^{-8} \text{ cm.} \quad . \quad . \quad . \quad . \quad (51)$$

The value found for  $l$  to satisfy the first theoretical condition for a face-centred lattice in (19) above is

$$l = 1.05 \times 10^{-8} \text{ cm.}, \quad . \quad . \quad . \quad (52)$$

which is so much smaller than either of the above values obtained from the density that both these lattices utterly fail to be satisfactory. This great discrepancy, however, is suggestive because the theory demands a very small distance between nearest atoms and the density demands a large average distance. The suggestion is that a group composed of a small number of atoms, probably four atoms, acts just like a single atom in a manner very analogous to, say, ammonium chloride, where  $\text{NH}_4$  behaves as if it were an element ammonium. This in combination with chlorine forms a cubic lattice, although the combination  $\text{NH}_4$  has no independent existence as such except as found in combination in some compound. In an analogous manner a group of four hydrogen atoms,  $\text{H}_4$ , has no independent existence as such because a hydrogen molecule,  $\text{H}_2$ , is unknown. It no doubt requires the presence of the surrounding atoms in a lattice to complete its stability.

If it is now assumed that such a group of four hydrogen atoms is arranged in the form of a regular tetrahedron, each with its axis pointing toward its centre, then the force upon the positive charge of one atom due to the other three may be found by the use of equation (2) or (4) above, in which

$$Z = \frac{1}{3} \sqrt{6}, \quad X = -\frac{1}{3} \sqrt{3}, \quad \cos \alpha = -\frac{1}{3},$$

$$\zeta = \frac{1}{9} \sqrt{6} \text{ (see (3))}, \quad -3Z\zeta + \cos \alpha = -1,$$

whence

$$F_{\frac{1}{3} \text{ atoms}} = \frac{e^2}{k} (-6) D r^{-3} . . . . . (53)$$

Equating this to (12), we have

$$\frac{e^2}{k} (-6) D r^{-3} = -\frac{e^2}{k} (30.7 \times 10^{24}) D, \quad . \quad . \quad . \quad (54)$$

whence

$$r^{-3} = 5.117 \times 10^{24} \text{ and } r = 0.58 \times 10^{-8} \text{ cm.} \quad (55)$$

There is evidently no equatorial force upon the positive charge of any one atom of the group because the other three atoms in the tetrahedron give rise to three equal forces in one plane making  $120^\circ$  with each other, thus giving a resultant of zero. Hence the equation (2) or (4), in the



derivation of which this equatorial displacement was assumed to be zero, applies to such a group of atoms as now supposed. The edge of the tetrahedron is, consequently, the very small value,  $0.58 \times 10^{-8}$  cm., which corresponds very closely with the distance between the two atoms of a single hydrogen molecule,  $H_2$ .

An application of equation (20) to the case will give a numerical value of  $D$ . We will not carry through a computation of  $D$  here, however, but merely note that both the first and second conditions are satisfied by such a tetrahedron of atoms.

The question immediately arises why will such an arrangement not form an independent molecule of  $H_4$ . The answer is that there is one condition that is not satisfied, and that is the turning moments of the forces, which must give a definite direction to each atom's axis. The sum of the turning moments of any three atoms of such a tetrahedron upon the fourth atom is zero, because each atom tries to turn its neighbour so that its axis comes into parallelism with itself. The effect of the three upon the one may be represented by three equal vectors in one plane making  $120^\circ$  with each other, whose sum is zero. There is, therefore, no directing influence upon any one atom to hold its axis in any particular direction, and as soon as one begins to turn the translational forces just computed are altered at once, and there is no stability. This rules out the tetrahedron as a stable molecule of  $H_4$  having an independent existence, but it does not prevent it from forming part of a large lattice of atoms, because this lattice may supply just the necessary requirement to satisfy the turning moments and thus give stability to the structure.

Now the distances between the atoms in such a tetrahedron are so small as compared with the distances between such groups in a cubic lattice, that the cube edge may be computed from the density of solid hydrogen as if there were one atom of four times the mass of the hydrogen atom at each corner of the cube. The mass of one elementary cube is then

$$m = 4 \times 1.66 \times 10^{-24} = 0.08 \text{ } l^3, \quad \dots \quad (56)$$

whence

$$l^3 = 83.0 \times 10^{-24} \quad \text{and} \quad l = 4.36 \times 10^{-8} \text{ cm.} \quad \dots \quad (57)$$

A possible form for the crystal of solid hydrogen may then be a cubic lattice of about  $4.36 \times 10^{-8}$  cm. on an edge, at the corners of which are groups of four hydrogen atoms

in the form of a regular tetrahedron of  $0.58 \times 10^{-8}$  cm. on an edge. This tetrahedron may be thought of as enclosed within a small cube whose edge is  $0.58 \times 10^{-8} / \sqrt{2} = 0.41 \times 10^{-8}$  cm., which is a little more than ten times smaller than the larger elementary cube given by (57).

To work out the forces upon one such group of atoms due to the whole lattice in detail by the use of the equations above given has not been attempted, but nevertheless the points that have been mentioned seem to warrant the suggestions made as to the form of the solid hydrogen lattice.

### Conclusion.

In this paper it is considered that an important real contact has been established between this atomic theory and some of the most reliable experimental measurements in the atomic realm, namely the facts that have been revealed in recent years by the use of X-rays in the analysis of crystals. The theory rings true at every point of contact. To arrive at this stage many steps have been required where the going must have seemed blind and the subject to be of an academic character, because the work could not be compared with any experimental data along the way. Now, however, the results seem certain to be of considerable practical value for chemistry.

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### LXXIII. A Natural Limit for the Sensibility of Galvanometers. By GUSTAF ISING \*.

IN the number of the Philosophical Magazine for Sept. 1925 W. J. H. Moll and H. C. Burger describe an interesting method of multiplying the sensibility of a galvanometer with the aid of their "Thermo-relay." When very high (25- to 100-fold) magnification of the sensibility of the primary Moll-galvanometer was employed, the registered curve showed small perpetual fluctuations of the zero-position, which by the authors are interpreted as due to microseismic perturbations. But, as shown in the following, there is reason to believe that the main part of these fluctuations were nothing else than the *Brownian fluctuations* of a suspended system, theoretically announced by M. v. Smoluchowsky †.

\* Communicated by the Author.

† *Phys. Zeitschr.* xiii. p. 1069 (1912).

I have earlier\* discussed the natural limit for the sensibility of some different kinds of instruments (electrometer, galvanometer, balance), which is determined, according to the theory, by these fluctuations, and shall in Parts I. and II. below repeat these considerations in so far as they concern galvanometers. With the aid of the obtained formulas then, in Part III., the curve (d) published by Moll and Burger on page 630 of the volume quoted will be examined.

## I.

Consider a movable system, the position of which is determined by a coordinate  $x$  and which is tied to the position  $x=x_0$  by a directional force  $A$ ; let  $\delta x = x - x_0$  denote the deviation from the zero-position at a certain instant  $\dagger$ . If the root-mean-square value of  $\delta x$  is denoted by  $\delta \bar{x}$ , according to Smoluchowsky (with other notations) the following relation holds:

$$\frac{1}{2} A \overline{\delta x^2} = \epsilon,$$

$$\text{or} \quad \delta \bar{x} = \sqrt{\frac{2\epsilon}{A}}, \quad . . . . . (1)$$

where  $\epsilon$  is the mean kinetic energy per degree of freedom of a molecule. At room temperature ( $18^\circ \text{C.}$ )  $\epsilon$  has the value  $2.00 \times 10^{-14}$  erg. If, for instance, a torsional system is

controlled by a directional force  $A = 10^{-6} \frac{\text{dyne} \times \text{cm.}}{\text{radian}^2}$ , eq. (1)

gives  $\delta \bar{x} = 2 \times 10^{-4}$  radian.

The sensibility ( $s$ ) of an instrument is now given by the quotient  $\frac{\delta x}{\delta i}$ , where  $\delta i$  is that change in a physical quantity  $i$  (current intensity, potential, etc.) which is to be measured by the instrument, and  $\delta x$  the deviation provoked by this change:

$$s = \frac{\delta x}{\delta i}.$$

As a rule the deviation is not directly given in "absolute"

\* G. Ising, *Undersökningar rörande elektrometrar*, i. p. 46 (1917); ii. p. 363 (1919). *Kosmos* p. 69 (1923). In Swedish.

† As a rule  $x$  denotes an angle. But, of course, the reasoning applies without change to any system with one degree of freedom, the position of which is determined by the parameter  $x$ ;  $A$  is then a directional force in generalized meaning:  $\frac{1}{2} A \overline{\delta x^2}$  giving the work (in ergs) necessary for a small deviation  $\delta x$ .

units  $\delta x$  (cms., radians, etc.) but in *scale-divisions*  $\delta x'$ ; one has

$$\delta x' = n \delta x,$$

where the factor of proportionality  $n$  may be termed the *magnification*. The sensibility, expressed as number of scale-divisions per unit change of  $i$ , is then

$$s' = \frac{\delta x'}{\delta i} = ns.$$

When the magnification has been made so great that the Brownian fluctuations of the zero point cover a visual angle which is easily discernible on the scale, there is, as a rule, no gain in pushing it further. The least deviation—we denote it by  $(\delta x)_{\min}$ —which one may be able to recognize, with confidence, as being really *provoked* (by a changem<sup>nt</sup>  $\delta i$ ) and not a mere Brownian fluctuation, may be estimated to about  $4\delta x$ :

$$(\delta x)_{\min} = 4\delta x. \quad (2)$$

This estimation is seen to be justified, if one supposes the magnification so high that  $\delta x' = \frac{1}{4}$  scale-division; the fluctuations on each side of the zero-position will then in the mean play over  $\frac{1}{2}$  division, and it seems reasonable to demand a deviation of one full scale-division, if it is to be recognized as provoked. Such a magnification should be amply sufficient; if one supposes good optical definition, so that tenths of a scale-division may be estimated, the limit for useful magnification will probably be reached, at least for trained observers, already when the mean Brownian fluctuation is only one-tenth of a scale-division to either side of the zero position. The smallest single deviation, which with fair probability may be distinguished from a Brownian fluctuation, is then about 0.4 scale-division\*.

## II.

We now proceed to deduce two known general formulas for the current- and potential-sensibility of galvanometers—pointing out that a similar calculus may be made for other kinds of instruments—and then we apply to them the preceding considerations of the Brownian fluctuations.

\* If one is able to follow for some time the fluctuations about a new position of equilibrium (=the provoked deviation), even a deviation *less* than four times the mean Brownian displacement may be established without doubt. In such a case it may be of advantage to carry the magnification somewhat further.

Mr. G. Ising on a Natural Limit for

The sensibility  $s = \frac{\delta x}{\delta i}$  of an instrument may be written as a quotient

$$\frac{\delta x}{\delta i} = \frac{B}{A}, \quad \dots \quad (3)$$

where the denominator  $A$  is the directional force and the numerator  $B$  a quantity such that  $B\delta i$  represents the deflecting moment, provoked by the change  $\delta i$ . For each kind of instrument (electrometer, galvanometer, balance, etc.) one is able to find certain general relations between the factors  $A$  and  $B$ , which allow interesting conclusions to be drawn concerning the sensibility of such instruments altogether irrespective of their special construction.

We consider here only the behaviour of galvanometers, and thus the letter  $i$  in the following always means current strength measured in electromagnetic units. Then we have generally

$$B = \frac{dN}{dx}, \quad \dots \quad (4)$$

where  $N$  denotes the flux of magnetic induction through the galvanometer-coils; when  $x$  changes, the magnets and the coils move relatively to each other, and the flux varies. A general relation between the  $B$  and  $A$  of any galvanometer is now obtained by supposing that the damping is *critical*, i. e., just sufficient to make the motion aperiodic, and further, that this damping is wholly brought about by the electromagnetic induction in the coils. In fact, a galvanometer will be almost useless for practical measurements if its damping is far from the critical one; the damping constant  $\lambda$  may not differ from the critical value  $\lambda = \omega_0$  (see below) by more than a factor of the magnitude 2 or 3. The neglect of the air-damping in comparison with the electromagnetic one is of minor real importance, and simplifies the formulas.

We introduce the notation:  $K$  moment of inertia of the moving system,  $p \frac{dx}{dt}$  moment of the frictional forces,  $T$  period of oscillation,  $T_0$  the period which would have been obtained without damping (i. e., for  $p=0$ ). The differential equation for the motion of the system may be written

$$\frac{d^2x}{dt^2} + 2\lambda \frac{dx}{dt} + (\lambda^2 + \omega^2)x = 0$$

where

$$\lambda = \frac{p}{2K} = \text{the damping constant,}$$

$$\omega = \frac{2\pi}{T} = \text{,, frequency,}$$

$$\omega_0 = \frac{2\pi}{T_0} = \sqrt{\frac{A}{K}} = \text{,, undamped } (\lambda = 0).$$

One has  $\lambda^2 + \omega^2 = \omega_0^2$ .

Further, if R is the resistance in the galvanometer circuit,

$$\lambda = \lambda_0 + \lambda_{e1} = \lambda_0 + \frac{B^2}{2KR}, \quad (5)$$

where  $\lambda_{e1}$  is the electromagnetic damping from the induction in the coils and  $\lambda_0$  other possible damping (for instance by the air friction). At the limit of aperiodicity  $\lambda = \omega_0$ , or

$$\lambda_0 + \frac{B^2}{2KR} = \omega_0,$$

which equation determines the value of B, when K, R,  $\omega_0$ , and  $\lambda_0$  are given. The greatest value of B, and therefore also the greatest sensibility, is obtained for  $\lambda_0 = 0$ . We make this assumption, as already mentioned, to simplify the formulas and thus get the system of equations

$$\left. \begin{aligned} \frac{\delta x}{\delta i} &= \frac{B}{A} = \text{the current-sensibility} \\ \omega_0 &= \sqrt{\frac{A}{K}} = \frac{B^2}{2KR} \end{aligned} \right\} \dots \dots (6)$$

Eliminating B and K, we get the current-sensibility  $s_i$ :

$$s_i = \frac{\delta x}{\delta i} = \sqrt{\frac{2R}{A\omega_0}}, \quad (7a)$$

and, dividing by R, the potential-sensibility  $s_v$ :

$$s_v = \frac{\delta x}{\delta v} = \sqrt{\frac{2}{AR\omega_0}}. \quad (7b)$$

These are the general formulas for the sensibility of galvanometers (at critical damping), mentioned at the beginning of Part II. By the way of their deduction it is evident that they apply as well to needle-galvanometers as to coil-galvanometers\*.

\* This must be remembered, if one would make a just comparison between these two kinds of galvanometers.

We now combine them with equations (1) and (2). Inserting in (7) for  $\delta x$  the value

$$(\delta x)_{\min} = 4\bar{\delta x} = 4\sqrt{\frac{2\epsilon}{A}},$$

we get the corresponding  $\delta i$  and  $\delta v$

$$\left. \begin{aligned} (\delta i)_{\min} &= 4\sqrt{\frac{\epsilon\omega_0}{R}} \\ (\delta v)_{\min} &= 4\sqrt{\epsilon\omega_0 R} \end{aligned} \right\}, \quad \dots \quad (8)$$

as the smallest changes in current strength and potential difference, respectively, which should be recognizable by one single observation.

If we introduce  $\omega_0 = \frac{2\pi}{T_0}$ ,  $\epsilon = 2.00 \times 10^{-14}$  and, instead of electromagnetic units, the practical units ampere, volt, and ohm, denoting by a dash quantities measured in them, we get

$$\left. \begin{aligned} (\delta i')_{\min} &= 4.48 \times 10^{-10} \frac{1}{\sqrt{T_0 R'}} \text{ amperes,} \\ (\delta v')_{\min} &= 4.48 \times 10^{-10} \sqrt{\frac{R'}{T_0}} \text{ volts} \end{aligned} \right\} \quad \dots \quad (9)$$

The current- or potential-changes that correspond to a deviation equal to the mean Brownian fluctuation are one-fourth of the values above, *e. g.* the change in potential difference

$$\bar{\delta v'} = 1.12 \times 10^{-10} \sqrt{\frac{R'}{T_0}} \text{ volts.} \quad \dots \quad (10)$$

Supposing, for instance,  $R' = 50$  ohms,  $T_0 = 2$  sec., we get

$$(\delta i')_{\min} = 4.48 \times 10^{-11} \text{ amp.}$$

$$(\delta v')_{\min} = 2.24 \times 10^{-9} \text{ volt.}$$

$$\bar{\delta v'} = 5.60 \times 10^{-10} \text{ ,,}$$

It is seen that the natural limit for a galvanometer's sensibility is almost surprisingly low. In the literature one finds several reports of (needle-) galvanometers with considerably higher sensibility. One may safely conjecture that in them the useful magnification was vastly surpassed or, in other words, that their reported high sensibility was made illusory by variations of the zero, perhaps already by variations caused by external disturbances but in any case by the Brownian fluctuations.

### III.

We now turn to the question whether these fluctuations have manifested themselves in the experiments of Moll and Burger. In order to examine this I photographed their curve (d), obtained with 100 times relay-multiplication\*, and magnified it still 10·3 times by projection. The middle-line of the then obtained rather thick curve-image was traced by a pencil, and the fluctuating distance ( $y$ ) of this line from a straight mean zero-line ( $x$ -axis) was measured for some hundred points on the curve. Three sections of the curve were treated separately, namely (1) the whole length on the left side of the great provoked deviation †; (2) the whole length between this and the small deviation; (3) about two-thirds of the length to the right of the small deviation ‡. The  $x$ -axis was drawn by eye to coincide as near as possible with the mean of the fluctuating curve; on section (1) it came out feebly inclined to the horizontal boundary-line of the figure, for sections (2) and (3) a common  $x$ -axis was drawn, which was very nearly horizontal.

For every millimetre on the  $x$ -axis the corresponding  $y$  was measured by a millimetre-scale (tenths estimated), and these  $y$ -values—reckoned positive upwards ( $y_+$ ) and negative downwards ( $y_-$ )—tabulated. The treatment of these figures will be clear from the following data concerning the longest section (2): number of measured points 390;  $\Sigma y_+ = 358\cdot0$  mm.;  $\Sigma y_- = -253\cdot0$ ; thus  $\Sigma y = 105\cdot0$  and the arithmetical mean

$$\bar{y} = \frac{\Sigma y}{390} = 0\cdot27 \text{ mm.}, \text{ which figure shows that the } x\text{-axis had}$$

happened to be drawn 0·27 mm. too low. This was corrected by adding -0·3 to every tabulated  $y$ -value; the figures thus obtained represent the fluctuations  $\Delta$ , the sum of their squares is  $\Sigma \Delta^2 = 1524\cdot6$  and the mean square value

$$\overline{\Delta^2} = \frac{1524\cdot6}{390} = 3\cdot91 \text{ mm}^2. \text{ In the same way it was found:}$$

for the section (1) with 190 measured points  $\bar{y} = -0\cdot18$  mm., and thus the  $y$ -correction = +0·2,  $\Sigma \Delta^2 = 778\cdot1$ , and  $\overline{\Delta^2} = 4\cdot10 \text{ mm}^2$ ; for the short section (3) with only 105 points  $\bar{y} = 0\cdot18$ ,  $\Sigma \Delta^2 = 343\cdot5$  and  $\overline{\Delta^2} = 3\cdot27 \text{ mm}^2$ .

\* Fig. I (d), Phil. Mag. l. p. 630 (1925).

† Compare fig. 1 (d) loc. cit.

‡ The last bit of the curve was left out because its mean course there shows an upward deflexion, easily visible in the enlargement, and probably due to some external disturbance.



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For all three sections together we have  $\Sigma \Delta^2 = 2646.2 \text{ mm}^2$ ,  
 $\overline{\Delta^2} = \frac{\Sigma \Delta^2}{685} = 3.86 \text{ mm}^2$ , and thus the mean fluctuation

$$\overline{\Delta} = \sqrt{\overline{\Delta^2}} = 1.97 \text{ mm.}$$

The great deviation on Moll's and Burger's curve, provoked by a potential difference of  $10 \times 10^{-8}$  volt, possessed on the enlarged curve a (mean) ordinate  $y = 213.5 \text{ mm.}$ ; the deviation of 1.97 mm. thus corresponds to

$$\frac{1.97}{213.5} \cdot 10^{-7} = 9.22 \times 10^{-10} \text{ volt,}$$

or  $\delta v'_{\text{observed}} = 9.22 \times 10^{-10} \text{ volt.}$

We will now compare this value with that calculated by formula (10). This calculation will, of course, be somewhat uncertain, as only approximate statements as to the value of  $R'$  and  $T_0$  are given: "this galvanometer has a time of indication of less than two seconds, its resistance is about 50 ohms" (on p. 629 of the quoted paper). It is probable, both from Dr. Moll's earlier description of the galvanometer\*, and from the published curves, that the galvanometer was used with critical damping; in this case a provoked deviation will reach its end-value to within  $\frac{1}{2}$  per cent. in a time  $= 1.18 T_0$ . Supposing this to be the meaning of the "time of indication" and putting it  $= 1.9 \text{ sec.}^\dagger$ , we get  $T_0 = 1.6 \text{ sec.}$  Assuming further, that the external resistance in the circuit was small, we may put  $R' = 50$ , and thus obtain

$$\overline{\delta v'}_{\text{calc.}} = 1.12 \times 10^{-10} \sqrt{\frac{50}{1.6}} = 6.3 \times 10^{-10} \text{ volt.}$$

This being about two-thirds of  $\delta v'_{\text{obs.}}$ , it seems fairly sure that the observed fluctuations in the main were Brownian fluctuations of the primary galvanometer, and only to some small extent due to external perturbations, perhaps micro-seismic ones such as supposed by Moll and Burger‡. This fact demonstrates very clearly what an admirable stability and freedom from disturbances the constructors have been able to give both to the galvanometer and to the thermo-relay, their combination approaching the theoretical limit of a galvanometer's sensibility.

Physical Laboratory of the University.  
 Stockholm, October, 1925.

\* Proc. Phys. Soc. xxxv. p. 253 (1923).

† The time of indication should be *less* than two sec.

‡ On the published curve (d), enlarged, there is scarcely to be found any support for the assumption of a regular *period* of the fluctuations.

LXXIV. *The Efficiency of  $\beta$ -ray Recoil of Radium C from Radium B.* By A. W. BARTON, M.A., B.Sc., Trinity College, Cambridge\*.

*Introductory.*

EXPERIMENTS on the  $\beta$ -ray recoil of Radium C from Radium B have previously been performed by Russ and Makower† and Muszkat‡. The former obtained efficiencies of about 0.1 per cent. from a surface of Radium B obtained by exposing a platinum disk to Radium Emanation in the usual way, and the latter using a surface of Radium B prepared by distillation in a vacuum claimed to have obtained values up to 50 per cent.

Recently Jacobsen§ has carried out a determination of the half-period of Radium C' by a method which depends for its success on obtaining an efficient  $\beta$ -ray recoil. In repeating this method with certain modifications, it was thought desirable first of all to investigate thoroughly the phenomenon of  $\beta$ -ray recoil, and the present experiments were performed with that aim in view. Although the conditions were similar the value of the efficiency obtained is considerably lower than that claimed by Muszkat, but as will be shown later it seems to be theoretically reasonable, and moreover an explanation is put forward to account for the discrepancy between the results of these experiments and those obtained by Muszkat.

*A Discussion of the Conditions necessary for an Efficient  $\beta$ -ray Recoil.*

When an atom of Radium B disintegrates emitting an electron the residual atom Radium C receives a velocity in the opposite direction. Taking  $1.7 \times 10^{10}$  cm. per sec. as a mean value of the velocity of the electron, that of the Radium C atom, the recoil atom, is  $4.4 \times 10^4$  cm. per sec., the corresponding energy being 0.4 volt. From Blackett's || work on the range of recoil atoms produced by impact with  $\alpha$ -particles, the range of these Radium C atoms can be estimated to be between  $10^{-6}$  cm. and  $10^{-8}$  cm. of air at atmospheric pressure. Obstructions of this order of thickness in the form of surface films of gas and tarnishing are almost certain to be present on the plate on which the Radium B,

\* Communicated by Professor Sir E. Rutherford, P.R.S.

† Phil. Mag. xix. p. 100 (1910).

‡ Phil. Mag. xxxix. p. 690 (1920).

§ Phil. Mag. xlvii. p. 23 (1924).

|| Proc. Roy. Soc. A, ciii. p. 62 (1923).

the parent atom, is deposited say by exposure to emanation, and would consequently prevent the recoil atoms from escaping from it and being collected on a plate near by. It is evident then that special conditions will have to be realized to obtain an efficient  $\beta$ -ray recoil. In discussing these conditions it is not necessary to argue from a theoretical standpoint, since they can be obtained empirically from the results of previous experiments which have a bearing on the problem.

Consider in the first place experiments on  $\alpha$ -ray recoil. Here the energy of recoil is of the order of 100,000 volts, and so whatever conditions are necessary for its detection must be realized in the case of  $\beta$ -ray recoil. Efficiencies up to 50 per cent. can be obtained in any case of  $\alpha$ -ray recoil provided that the parent atom is deposited on a clean well-polished surface. (An efficiency of 100 per cent. is to be taken to mean that the maximum theoretical number of recoil atoms has been collected.) Any tarnishing of the surface causes a considerable decrease in efficiency. But in some experiments by the author on the recoil of Thorium D from Thorium C efficiencies of 100 per cent. were obtained. The Thorium C was first deposited on a nickel wire by von Lerch's method and then distilled in air from this wire on to a polished brass cylinder, from which the recoil atoms were subsequently collected in a vacuum. The first condition to be satisfied, then, to obtain an efficient  $\beta$ -ray recoil is that the surface of the parent atom must be prepared by distilling it on to a polished plate.

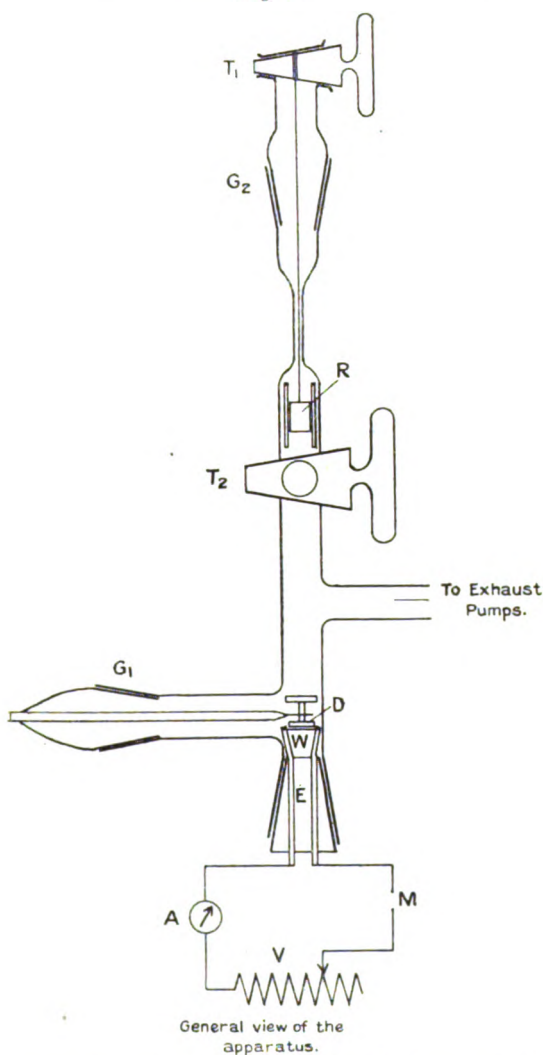
Secondly, consider the experiments on the photoelectric effect with visible radiation where the energy of the electrons is of the same order as that of the  $\beta$ -ray recoil atoms, about one volt. Here the escape of the electrons was greatly impeded unless a "clean" surface was used (a clean surface is one which is prepared in a vacuum and is never afterwards exposed to the atmosphere either before or during use). This will also be true of  $\beta$ -ray recoil atoms, and therefore the second condition to be satisfied to obtain an efficient  $\beta$ -ray recoil is that the parent atom must be prepared in a vacuum and never be exposed to the air before or during recoil.

The simplest way of combining these two conditions in practice is to distil the parent atom from a wire on to a plate close by in a vacuum and to collect the recoil atoms from that plate, which is not exposed to the air until the recoil is stopped. The pressure of the air should be less than  $10^{-3}$  mm. of mercury, since at this pressure the mean free

path of the recoil atoms would be about 7 cm., and so one which has escaped from the surface of the parent atom would be certain to reach a plate a millimetre or so away.

*Description of the Apparatus and Experimental Details.*

Fig. 1.



The arrangement of the apparatus is shown in figs. 1, 2, and 3. Radium Active Deposit is obtained on the platinum

TABLE XII. (continued).

No. Sphere.	Radius Sphere.	No. Plane.	No. Circle.	Cos $\alpha$ .	No. Atoms, Circle.	No. Atoms, Sphere.	Total Atoms.	$\Sigma(-3ZZ + \cos \alpha)p^{-2}$ .
10	$\frac{1}{2} \sqrt{10} l$	+2	4	$-\frac{1}{3}$	6			
"	" "	+4	3	"	6	24	146	-73.4643
11	$\frac{1}{4} \sqrt{43}$	-3	4	"	6			
"	" "	-1	5	1	3			
"	" "	+5	1	$-\frac{1}{3}$	3	12	158	-71.6907
12	$\sqrt{3}$	+2	5	1	3			
"	" "	+6	0	1	1	8	166	"
13	$\frac{1}{4} \sqrt{51}$	-5	2	$-\frac{1}{3}$	6			
"	" "	-3	5	1	3			
"	" "	-1	6	$-\frac{1}{3}$	6			
"	" "	+3	4	"	6			
"	" "	+5	2	1	3	24	190	-72.9035
14	$\frac{1}{2} \sqrt{14}$	0	4	$-\frac{1}{3}$	12			
"	" "	+2	6	"	6			
"	" "	+4	4	"	6			
"	" "	+6	1	"	6	48	238	-73.6017
15	$\frac{1}{4} \sqrt{59}$	-7	1	"	3			
"	" "	-5	3	1	6			
"	" "	-3	6	$-\frac{1}{3}$	6			
"	" "	+1	4	"	12			
"	" "	+3	5	1	3			
"	" "	+5	3	$-\frac{1}{3}$	6	36	274	-74.2527
16	2	+4	5	1	3	6	280	"
17	$\frac{1}{4} \sqrt{67}$	-7	2	1	3			
"	" "	-1	7	$-\frac{1}{3}$	3			
"	" "	+3	6	"	6	12	292	-75.6740

TABLE XII. (continued).

No. Sphere.	Radius Sphere.	No. Plane.	No. Circle.	Cos $\alpha$ .	No. Atoms, Circle.	No. Atoms, Sphere.	Total Atoms.	$\Sigma(-3Z\epsilon + \cos \alpha)p^{-3}$ .
18	$\frac{3}{2}\sqrt{2} l$	0	5	$-\frac{1}{3}$	6			
"	" "	+2	7	"	3			
"	" "	+4	6	"	6			
"	" "	+6	2	"	6	36	328	-73.7186
19	$\frac{5}{4}\sqrt{3}$	-7	3	"	6			
"	" "	-3	7	"	3			
"	" "	-1	8	"	6			
"	" "	+1	5	$-\frac{1}{3}$	6			
"	" "	+5	4	"	6			
"	" "	+7	0	1	1	28	356	-72.6886
20	$\sqrt{5}$	+2	8	1	6			
"	" "	+6	3	1	6	24	380	"
21	$\frac{1}{4}\sqrt{83}$	-5	4	$-\frac{1}{3}$	12			
"	" "	-3	8	1	6			
"	" "	-1	9	$-\frac{1}{3}$	6			
"	" "	+3	7	"	3			
"	" "	+5	5	1	3			
"	" "	+7	1	$-\frac{1}{3}$	6	36	416	-72.1216
22	$\frac{1}{2}\sqrt{22}$	+2	9	"	6			
"	" "	+4	7	"	3			
"	" "	+8	1	"	3	24	440	-72.6855
23	$\frac{1}{4}\sqrt{91}$	-7	4	"	6			
"	" "	-3	9	"	6			
"	" "	+3	8	1	6			
"	" "	+5	6	$-\frac{1}{3}$	6	24	464	-72.1410
24	$\sqrt{6}$	0	6	1	6			
"	" "	+4	8	1	6			
"	" "	+8	2	1	3	24	488	"

and circle by circle in these planes. The last column gives the important total summation of  $f_1$  of equation (10) when multiplied by  $p^{-3}$ , where  $p=r/l$ , for all the spheres from the first to the given sphere inclusive. By this last column it is seen that the first sphere gives the largest sum, but that for a very accurate value for an infinite lattice probably more than 24 spheres should be computed.

Table XIII. gives the sum of  $p^{-4}f_2$ , where  $f_2$  is given by (11) above. This Table includes but 6 spheres and 70 atoms. The more rapid decrease in this sum per sphere with increasing sphere number is due to the higher order of the term,  $r^{-4}$  instead of  $r^{-3}$  above, so that an approximate value for an infinite lattice is obtained from 6 spheres.

TABLE XIII.  
Diamond Lattice.

No. sphere.	No. atoms.	$\Sigma p^{-4}f_2$ sphere.	$\Sigma p^{-4}f_2$ total.
1	4	-44.949	-44.949
2	12	0	-44.949
3	12	-10.952	-55.901
4	6	0	-55.901
5	12	+0.3515	55.55
6	24	0	-55.55
Total..... 70			

By the use of the sums in Tables XII. and XIII. it is possible to write down the sum of equation (29) for the whole diamond lattice. The total force upon the positive charge of the selected carbon atom at the origin due to the whole surrounding lattice of carbon atoms is, therefore, approximately

$$F = \frac{e^2}{k} \{ 36(-72.14)(D+H)l^{-3} + 108(-55.55)[(b^2+h^2)-\rho a^2]l^{-4} \dots \}. \quad (31)$$

Diamond lattice  
on 3 + charges.

The force upon just one positive charge of one of the

alpha-particles of one carbon atom is, therefore, one third of the above force, and this may be equated to the expression in (12) above because the same reasoning applies here as there, the value of  $\rho_z$  having been derived from the properties of the electron itself. Hence we find the equation representing the first condition that must be satisfied by the carbon lattice, namely

$$-865\cdot68(D+H)l^{-3}-1999\cdot8[(b^2+h'^2)-\rho a^2]l^{-4} \\ = -30\cdot7 \times 10^{24}D. \quad (32)$$

The second condition is that the sum of the forces of all atoms in the lattice upon the whole of each and every atom in the lattice shall be equal to zero. If the lattice were constructed of hydrogen atoms the sum of the forces given by (20) above must be zero, but if constructed of carbon atoms the sum of the forces given by (30) must vanish. Since both these equations involve the same functions of  $X$ ,  $Y$ , and  $Z$ , it seems best to consider them together in order that their differences may be emphasized. The sums of the functions  $f_3$  to  $f_{10}$  given in (21) to (28) are found for the diamond lattice to be as follows:—Since  $f_3$  is the coefficient of an  $r^{-4}$  term, it has been summed for six concentric spheres including 70 atoms, but  $f_4$ ,  $f_5$ , and  $f_6$  have been summed for only three spheres, 28 atoms, these being coefficients of an  $r^{-5}$  term; while  $f_7$  to  $f_{10}$  have been summed for but two spheres, 16 atoms. We find for the diamond form of lattice

$$\Sigma f_3 r^{-4} = 89\cdot218 l^{-4}, \quad . \quad . \quad . \quad (33)$$

$$\Sigma f_4 r^{-5} = -1022\cdot597 l^{-5}, \quad . \quad . \quad . \quad (34)$$

$$\Sigma (f_5 + f_6) r^{-5} = -1015\cdot575 l^{-5}, \quad . \quad . \quad . \quad (35)$$

$$\Sigma f_7 r^{-6} = -2217\cdot496 l^{-6}, \quad . \quad . \quad . \quad (36)$$

$$\Sigma (f_8 + 2f_9) r^{-6} = 1917\cdot83 l^{-6}, \quad . \quad . \quad . \quad (37)$$

$$\Sigma f_{10} r^{-6} = 775\cdot374 l^{-6}, \quad . \quad . \quad . \quad (38)$$

Substituting these summations in (20) gives the force of the whole lattice of hydrogen atoms upon the one hydrogen atom as

$$F_s = \frac{3e^2}{k} \{ 89\cdot218 D^2 l^{-4} - 1022\cdot597 b^2 D l^{-5} \\ + 507\cdot788 \rho a^2 D l^{-5} - 11087\cdot48 b^4 l^{-6} \\ + 4794\cdot58 \rho a^2 b^2 l^{-6} - 1938\cdot44 \rho^2 a^4 l^{-6} \} = 0. \\ . \quad . \quad . \quad (39)$$





values found for D and H, the small differences between the upper and lower distances should vary considerably from one form to another, since they are connected with the energies of formation and dissociation of the molecule in question. It may be seen from a study of the manner in which the forces act upon the electrons shown by the drawing of the model of the carbon atom in fig. 3 that H will be approximately the same proportion of D that  $h'$  is of  $b$ . Let us assume for a first approximation, which will be slightly modified as we proceed, that this ratio is exactly one half. If so, equations (32) and (40) contain only D and  $l$  as the unknown quantities, since  $b^2$  and  $\rho a^2$  are known numerically, as given in (41) above. Consequently they may be solved very readily for both the unknown quantities, D and  $l$ , since under this hypothesis (40) reduces to a quadratic in terms of  $Dl$  similar to (42). The value obtained for the cube edge,  $l$ , however, under the supposition that  $h' = 0.5b$ , does not come out exactly equal to the experimental value of  $l$  for the diamond. This ratio assumed as 0.5 above requires to be slightly altered to approximately

$$h' = 0.42b \quad \text{and} \quad H = 0.42D, \quad . \quad . \quad . \quad (44)$$

when the solution of the two simultaneous equations (32) and (40) gives exactly

$$l = 3.56 \times 10^{-8} \text{ cm.} \quad \text{and} \quad D = -11.9 \times 10^{-18} \text{ cm.}, \quad (45)$$

the former being the experimental value for the cube edge. In fact, when  $l = 3.56 \times 10^{-8} \text{ cm.}$  and  $h'$  and H as in (44) are substituted in (32), we find immediately

$$D = -11.92 \times 10^{-18} \text{ cm.} \quad . \quad . \quad . \quad (46)$$

When they are substituted in (40) we have the quadratic equation

$$D^2 + 7.4296 \times 10^{-18}D = 52.88 \times 10^{-36}, \quad . \quad . \quad (47)$$

from which

$$D = -11.88 \times 10^{-18} \text{ cm.} \quad \text{or} \quad +4.45 \times 10^{-18} \text{ cm.} \quad (48)$$

The negative values of D in (46) and (48) are very closely the same, and a value of  $h'$  very slightly in excess of  $0.42b$  will make the two values of D identical. This value for D incidentally is not far different from that found for the hydrogen molecule in the previous paper\*, namely  $14.47 \times 10^{-18} \text{ cm.}$

Both conditions are, therefore, perfectly satisfied by the

\* Phil. Mag. May 1925, p. 882, eq. (66).

form of the diamond lattice, by its absolute dimensions, and by the model of the carbon atom shown in fig. 3, and we may conclude on theoretical grounds alone that the carbon atom may form such a crystal.

The negative value of  $D$  shows that the force upon the positive charge is positive according to (12), that is in an upward direction away from the base and toward the apex of the regular tetrahedron of atoms forming the first surrounding sphere in the lattice. Hence the electron on the side of this apex is the one that is compressed, while that on the side toward the base is the one that is expanded.

This completes the account of the diamond, and we would naturally turn next to graphite for still further confirmation of these ideas. Graphite, however, does not come under the head of the cubic or isometric system of crystals, and as yet its study has not been completed. There is the problem of determining the directions of the axes of each atom in the crystal before any of the above equations for the carbon atom may be applied. We shall conclude the paper by making some suggestions as to a possible form for a crystal of solid hydrogen.

### *The Hydrogen Lattice.*

It has been shown above that hydrogen will not crystallize in the form of any one of the four lattices of the cubic system considered. The question remains, "how does it crystallize?" The investigation has not proceeded far enough to enable this question to be answered with definiteness, but there are certain indications worth noting. The first of these is the measured density of liquid hydrogen. Dewar gives it as 0.070 at  $-252^{\circ}\text{C}.$ , but the writer has found no record of the density of solid hydrogen. Lacking this, it may be assumed that the density is roughly 0.08, because the ratio of 8/7 is not far from that which the solid to the liquid form has in a number of the elements.

If hydrogen formed a simple cubic lattice, which it does not, this density would give the cube edge as

$$l = 2.75 \times 10^{-8} \text{ cm.}, \quad . \quad . \quad . \quad . \quad . \quad (49)$$

but if it formed a face-centred lattice the same density would give

$$l = 4.36 \times 10^{-8} \text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad (50)$$

and the distance between nearest atoms would be

$$\frac{1}{2} \sqrt{2}l = 3.08 \times 10^{-8} \text{ cm.} \quad . \quad . \quad . \quad . \quad (51)$$

The value found for  $l$  to satisfy the first theoretical condition for a face-centred lattice in (19) above is

$$l = 1.05 \times 10^{-8} \text{ cm.}, \quad . \quad . \quad . \quad (52)$$

which is so much smaller than either of the above values obtained from the density that both these lattices utterly fail to be satisfactory. This great discrepancy, however, is suggestive because the theory demands a very small distance between nearest atoms and the density demands a large average distance. The suggestion is that a group composed of a small number of atoms, probably four atoms, acts just like a single atom in a manner very analogous to, say, ammonium chloride, where  $\text{NH}_4$  behaves as if it were an element ammonium. This in combination with chlorine forms a cubic lattice, although the combination  $\text{NH}_4$  has no independent existence as such except as found in combination in some compound. In an analogous manner a group of four hydrogen atoms,  $\text{H}_4$ , has no independent existence as such because a hydrogen molecule,  $\text{H}_2$ , is unknown. It no doubt requires the presence of the surrounding atoms in a lattice to complete its stability.

If it is now assumed that such a group of four hydrogen atoms is arranged in the form of a regular tetrahedron, each with its axis pointing toward its centre, then the force upon the positive charge of one atom due to the other three may be found by the use of equation (2) or (4) above, in which

$$Z = \frac{1}{3} \sqrt{6}, \quad X = -\frac{1}{3} \sqrt{3}, \quad \cos \alpha = -\frac{1}{3},$$

$$\zeta = \frac{1}{9} \sqrt{6} \text{ (see (3))}, \quad -3Z\zeta + \cos \alpha = -1,$$

whence

$$F_z = \frac{e^2}{k} (-6) D r^{-3} \quad . \quad . \quad . \quad (53)$$

3 atoms.

Equating this to (12), we have

$$\frac{e^2}{k} (-6) D r^{-3} = -\frac{e^2}{k} (30.7 \times 10^{24}) D, \quad . \quad . \quad . \quad (54)$$

whence

$$r^{-3} = 5.117 \times 10^{24} \text{ and } r = 0.58 \times 10^{-8} \text{ cm.} \quad (55)$$

There is evidently no equatorial force upon the positive charge of any one atom of the group because the other three atoms in the tetrahedron give rise to three equal forces in one plane making  $120^\circ$  with each other, thus giving a resultant of zero. Hence the equation (2) or (4), in the

derivation of which this equatorial displacement was assumed to be zero, applies to such a group of atoms as now supposed. The edge of the tetrahedron is, consequently, the very small value,  $0.58 \times 10^{-8}$  cm., which corresponds very closely with the distance between the two atoms of a single hydrogen molecule,  $H_2$ .

An application of equation (20) to the case will give a numerical value of  $D$ . We will not carry through a computation of  $D$  here, however, but merely note that both the first and second conditions are satisfied by such a tetrahedron of atoms.

The question immediately arises why will such an arrangement not form an independent molecule of  $H_4$ . The answer is that there is one condition that is not satisfied, and that is the turning moments of the forces, which must give a definite direction to each atom's axis. The sum of the turning moments of any three atoms of such a tetrahedron upon the fourth atom is zero, because each atom tries to turn its neighbour so that its axis comes into parallelism with itself. The effect of the three upon the one may be represented by three equal vectors in one plane making  $120^\circ$  with each other, whose sum is zero. There is, therefore, no directing influence upon any one atom to hold its axis in any particular direction, and as soon as one begins to turn the translational forces just computed are altered at once, and there is no stability. This rules out the tetrahedron as a stable molecule of  $H_4$  having an independent existence, but it does not prevent it from forming part of a large lattice of atoms, because this lattice may supply just the necessary requirement to satisfy the turning moments and thus give stability to the structure.

Now the distances between the atoms in such a tetrahedron are so small as compared with the distances between such groups in a cubic lattice, that the cube edge may be computed from the density of solid hydrogen as if there were one atom of four times the mass of the hydrogen atom at each corner of the cube. The mass of one elementary cube is then

$$m = 4 \times 1.66 \times 10^{-24} = 0.08 \, l^3, \quad \dots \quad (56)$$

whence

$$l^3 = 83.0 \times 10^{-24} \quad \text{and} \quad l = 4.36 \times 10^{-8} \text{ cm.} \quad \dots \quad (57)$$

A possible form for the crystal of solid hydrogen may then be a cubic lattice of about  $4.36 \times 10^{-8}$  cm. on an edge, at the corners of which are groups of four hydrogen atoms

in the form of a regular tetrahedron of  $0.58 \times 10^{-8}$  cm. on an edge. This tetrahedron may be thought of as enclosed within a small cube whose edge is  $0.58 \times 10^{-8} / \sqrt{2} = 0.41 \times 10^{-8}$  cm., which is a little more than ten times smaller than the larger elementary cube given by (57).

To work out the forces upon one such group of atoms due to the whole lattice in detail by the use of the equations above given has not been attempted, but nevertheless the points that have been mentioned seem to warrant the suggestions made as to the form of the solid hydrogen lattice.

### Conclusion.

In this paper it is considered that an important real contact has been established between this atomic theory and some of the most reliable experimental measurements in the atomic realm, namely the facts that have been revealed in recent years by the use of X-rays in the analysis of crystals. The theory rings true at every point of contact. To arrive at this stage many steps have been required where the going must have seemed blind and the subject to be of an academic character, because the work could not be compared with any experimental data along the way. Now, however, the results seem certain to be of considerable practical value for chemistry.

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### LXXIII. A Natural Limit for the Sensibility of Galvanometers. By GUSTAF ISING \*.

IN the number of the Philosophical Magazine for Sept. 1925 W. J. H. Moll and H. C. Burger describe an interesting method of multiplying the sensibility of a galvanometer with the aid of their "Thermo-relay." When very high (25- to 100-fold) magnification of the sensibility of the primary Moll-galvanometer was employed, the registered curve showed small perpetual fluctuations of the zero-position, which by the authors are interpreted as due to microseismic perturbations. But, as shown in the following, there is reason to believe that the main part of these fluctuations were nothing else than the *Brownian fluctuations* of a suspended system, theoretically announced by M. v. Smoluchowsky †.

\* Communicated by the Author.

† *Phys. Zeitschr.* xiii. p. 1069 (1912).

I have earlier\* discussed the natural limit for the sensibility of some different kinds of instruments (electrometer, galvanometer, balance), which is determined, according to the theory, by these fluctuations, and shall in Parts I. and II. below repeat these considerations in so far as they concern galvanometers. With the aid of the obtained formulas then, in Part III., the curve (*d*) published by Moll and Burger on page 630 of the volume quoted will be examined.

## I.

Consider a movable system, the position of which is determined by a coordinate  $x$  and which is tied to the position  $x=x_0$  by a directional force  $A$ ; let  $\delta x = x - x_0$  denote the deviation from the zero-position at a certain instant †. If the root-mean-square value of  $\delta x$  is denoted by  $\delta \bar{x}$ , according to Smoluchowsky (with other notations) the following relation holds:

$$\frac{1}{2} A \delta \bar{x}^2 = \epsilon,$$

$$\text{or} \quad \delta \bar{x} = \sqrt{\frac{2\epsilon}{A}}, \quad . . . . . (1)$$

where  $\epsilon$  is the mean kinetic energy per degree of freedom of a molecule. At room temperature ( $18^\circ \text{C.}$ )  $\epsilon$  has the value  $2.00 \times 10^{-14}$  erg. If, for instance, a torsional system is controlled by a directional force  $A = 10^{-6} \frac{\text{dyne} \times \text{cm.}}{\text{radian}^2}$ , eq. (1) gives  $\delta \bar{x} = 2 \times 10^{-4}$  radian.

The sensibility ( $s$ ) of an instrument is now given by the quotient  $\frac{\delta x}{\delta i}$ , where  $\delta i$  is that change in a physical quantity  $i$  (current intensity, potential, etc.) which is to be measured by the instrument, and  $\delta x$  the deviation provoked by this change:

$$s = \frac{\delta x}{\delta i}.$$

As a rule the deviation is not directly given in "absolute"

\* G. Ising, *Undersökningar rörande elektrometrar*, i. p. 46 (1917); ii. p. 363 (1919). *Kosmos* p. 69 (1923). In Swedish.

† As a rule  $x$  denotes an angle. But, of course, the reasoning applies without change to any system with one degree of freedom, the position of which is determined by the parameter  $x$ ;  $A$  is then a directional force in generalized meaning:  $\frac{1}{2} A \delta x^2$  giving the work (in ergs) necessary for a small deviation  $\delta x$ .

units  $\delta x$  (cms., radians, etc.) but in *scale-divisions*  $\delta x'$ ; one has

$$\delta x' = n \delta x,$$

where the factor of proportionality  $n$  may be termed the *magnification*. The sensibility, expressed as number of scale-divisions per unit change of  $i$ , is then

$$s' = \frac{\delta x'}{\delta i} = ns.$$

When the magnification has been made so great that the Brownian fluctuations of the zero point cover a visual angle which is easily discernible on the scale, there is, as a rule, no gain in pushing it further. The least deviation—we denote it by  $(\delta x)_{\min}$ —which one may be able to recognize, with confidence, as being really *provoked* (by a change in  $i$ ) and not a mere Brownian fluctuation, may be estimated to about  $4\delta x$ :

$$(\delta x)_{\min} = 4\delta x. \quad (2)$$

This estimation is seen to be justified, if one supposes the magnification so high that  $\delta x' = \frac{1}{4}$  scale-division; the fluctuations on each side of the zero-position will then in the mean play over  $\frac{1}{2}$  division, and it seems reasonable to demand a deviation of one full scale-division, if it is to be recognized as provoked. Such a magnification should be amply sufficient; if one supposes good optical definition, so that tenths of a scale-division may be estimated, the limit for useful magnification will probably be reached, at least for trained observers, already when the mean Brownian fluctuation is only one-tenth of a scale-division to either side of the zero position. The smallest single deviation, which with fair probability may be distinguished from a Brownian fluctuation, is then about 0.4 scale-division\*.

## II.

We now proceed to deduce two known general formulas for the current- and potential-sensibility of galvanometers—pointing out that a similar calculus may be made for other kinds of instruments—and then we apply to them the preceding considerations of the Brownian fluctuations.

\* If one is able to follow for some time the fluctuations about a new position of equilibrium (=the provoked deviation), even a deviation *less* than four times the mean Brownian displacement may be established without doubt. In such a case it may be of advantage to carry the magnification somewhat further.



Mr. G. Ising on a Natural Limit for

The sensibility  $s = \frac{\delta x}{\delta i}$  of an instrument may be written as a quotient

$$\frac{\delta x}{\delta i} = \frac{B}{A}, \quad \dots \dots \dots (3)$$

where the denominator  $A$  is the directional force and the numerator  $B$  a quantity such that  $B\delta i$  represents the deflecting moment, provoked by the change  $\delta i$ . For each kind of instrument (electrometer, galvanometer, balance, etc.) one is able to find certain general relations between the factors  $A$  and  $B$ , which allow interesting conclusions to be drawn concerning the sensibility of such instruments altogether irrespective of their special construction.

We consider here only the behaviour of galvanometers, and thus the letter  $i$  in the following always means current strength measured in electromagnetic units. Then we have generally

$$B = \frac{dN}{dx}, \quad \dots \dots \dots (4)$$

where  $N$  denotes the flux of magnetic induction through the galvanometer-coils; when  $x$  changes, the magnets and the coils move relatively to each other, and the flux varies. A general relation between the  $B$  and  $A$  of any galvanometer is now obtained by supposing that the damping is *critical*, i. e., just sufficient to make the motion aperiodic, and further, that this damping is wholly brought about by the electromagnetic induction in the coils. In fact, a galvanometer will be almost useless for practical measurements if its damping is far from the critical one; the damping constant  $\lambda$  may not differ from the critical value  $\lambda = \omega_0$  (see below) by more than a factor of the magnitude 2 or 3. The neglect of the air-damping in comparison with the electromagnetic one is of minor real importance, and simplifies the formulas.

We introduce the notation:  $K$  moment of inertia of the moving system,  $p \frac{dx}{dt}$  moment of the frictional forces,  $T$  period of oscillation,  $T_0$  the period which would have been obtained without damping (i. e., for  $p=0$ ). The differential equation for the motion of the system may be written

$$\frac{d^2x}{dt^2} + 2\lambda \frac{dx}{dt} + (\lambda^2 + \omega^2)x = 0$$

where

$$\lambda = \frac{p}{2K} = \text{the damping constant,}$$

$$\omega = \frac{2\pi}{T} = \text{,, frequency,}$$

$$\omega_0 = \frac{2\pi}{T_0} = \sqrt{\frac{A}{K}} = \text{,, undamped } (\lambda = 0).$$

One has  $\lambda^2 + \omega^2 = \omega_0^2$ .

Further, if  $R$  is the resistance in the galvanometer circuit,

$$\lambda = \lambda_0 + \lambda_{el} = \lambda_0 + \frac{B^2}{2KR}, \quad . \quad . \quad . \quad . \quad (5)$$

where  $\lambda_{el}$  is the electromagnetic damping from the induction in the coils and  $\lambda_0$  other possible damping (for instance by the air friction). At the limit of aperiodicity  $\lambda = \omega_0$ , or

$$\lambda_0 + \frac{B^2}{2KR} = \omega_0,$$

which equation determines the value of  $B$ , when  $K$ ,  $R$ ,  $\omega_0$ , and  $\lambda_0$  are given. The greatest value of  $B$ , and therefore also the greatest sensibility, is obtained for  $\lambda_0 = 0$ . We make this assumption, as already mentioned, to simplify the formulas and thus get the system of equations

$$\left. \begin{aligned} \frac{\delta x}{\delta i} &= \frac{B}{A} = \text{the current-sensibility} \\ \omega_0 &= \sqrt{\frac{A}{K}} = \frac{B^2}{2KR} \end{aligned} \right\} . . . . (6)$$

Eliminating  $B$  and  $K$ , we get the current-sensibility  $s_i$ :

$$s_i = \frac{\delta x}{\delta i} = \sqrt{\frac{2R}{A\omega_0}}, \quad . . . . (7a)$$

and, dividing by  $R$ , the potential-sensibility  $s_v$ :

$$s_v = \frac{\delta x}{\delta v} = \sqrt{\frac{2}{AR\omega_0}} . . . . (7b)$$

These are the general formulas for the sensibility of galvanometers (at critical damping), mentioned at the beginning of Part II. By the way of their deduction it is evident that they apply as well to needle-galvanometers as to coil-galvanometers\*.

\* This must be remembered, if one would make a just comparison between these two kinds of galvanometers.

We now combine them with equations (1) and (2). Inserting in (7) for  $\delta x$  the value

$$(\delta x)_{\min} = 4\bar{\delta}x = 4\sqrt{\frac{2\epsilon}{A}},$$

we get the corresponding  $\delta i$  and  $\delta v$

$$\left. \begin{aligned} (\delta i)_{\min} &= 4\sqrt{\frac{\epsilon\omega_0}{R}} \\ (\delta v)_{\min} &= 4\sqrt{\epsilon\omega_0 R} \end{aligned} \right\}, \quad . . . . (8)$$

as the smallest changes in current strength and potential difference, respectively, which should be recognizable by one single observation.

If we introduce  $\omega_0 = \frac{2\pi}{T_0}$ ,  $\epsilon = 2.00 \times 10^{-14}$  and, instead of electromagnetic units, the practical units ampere, volt, and ohm, denoting by a dash quantities measured in them, we get

$$\left. \begin{aligned} (\delta i')_{\min} &= 4.48 \times 10^{-10} \frac{1}{\sqrt{T_0 R'}} \text{ amperes,} \\ (\delta v')_{\min} &= 4.48 \times 10^{-10} \sqrt{\frac{R'}{T_0}} \text{ volts} \end{aligned} \right\} . . . (9)$$

The current- or potential-changes that correspond to a deviation equal to the mean Brownian fluctuation are one-fourth of the values above, *e. g.* the change in potential difference

$$\bar{\delta}v' = 1.12 \times 10^{-10} \sqrt{\frac{R'}{T_0}} \text{ volts.} \quad . . . (10)$$

Supposing, for instance,  $R' = 50$  ohms,  $T_0 = 2$  sec., we get

$$(\delta i')_{\min} = 4.48 \times 10^{-11} \text{ amp.}$$

$$(\delta v')_{\min} = 2.24 \times 10^{-9} \text{ volt.}$$

$$\bar{\delta}v' = 5.60 \times 10^{-10} \text{ ,,}$$

It is seen that the natural limit for a galvanometer's sensibility is almost surprisingly low. In the literature one finds several reports of (needle-) galvanometers with considerably higher sensibility. One may safely conjecture that in them the useful magnification was vastly surpassed or, in other words, that their reported high sensibility was made illusory by variations of the zero, perhaps already by variations caused by external disturbances but in any case by the Brownian fluctuations.

### III.

We now turn to the question whether these fluctuations have manifested themselves in the experiments of Moll and Burger. In order to examine this I photographed their curve (*d*), obtained with 100 times relay-multiplication\*, and magnified it still 10·3 times by projection. The middle-line of the then obtained rather thick curve-image was traced by a pencil, and the fluctuating distance (*y*) of this line from a straight mean zero-line (*x*-axis) was measured for some hundred points on the curve. Three sections of the curve were treated separately, namely (1) the whole length on the left side of the great provoked deviation †; (2) the whole length between this and the small deviation; (3) about two-thirds of the length to the right of the small deviation ‡. The *x*-axis was drawn by eye to coincide as near as possible with the mean of the fluctuating curve; on section (1) it came out feebly inclined to the horizontal boundary-line of the figure, for sections (2) and (3) a common *x*-axis was drawn, which was very nearly horizontal.

For every millimetre on the *x*-axis the corresponding *y* was measured by a millimetre-scale (tenths estimated), and these *y*-values—reckoned positive upwards (*y*<sub>+</sub>) and negative downwards (*y*<sub>-</sub>)—tabulated. The treatment of these figures will be clear from the following data concerning the longest section (2): number of measured points 390;  $\Sigma y_+ = 358\cdot0$  mm.;  $\Sigma y_- = -253\cdot0$ ; thus  $\Sigma y = 105\cdot0$  and the arithmetical mean

$$\bar{y} = \frac{\Sigma y}{390} = 0\cdot27 \text{ mm.}, \text{ which figure shows that the } x\text{-axis had}$$

happened to be drawn 0·27 mm. too low. This was corrected by adding +0·3 to every tabulated *y*-value; the figures thus obtained represent the fluctuations  $\Delta$ , the sum of their squares is  $\Sigma \Delta^2 = 1524\cdot6$  and the mean square value

$$\overline{\Delta^2} = \frac{1524\cdot6}{390} = 3\cdot91 \text{ mm}^2. \text{ In the same way it was found:}$$

for the section (1) with 190 measured points  $\bar{y} = -0\cdot18$  mm., and thus the *y*-correction = +0·2,  $\Sigma \Delta^2 = 778\cdot1$ , and  $\overline{\Delta^2} = 4\cdot10 \text{ mm}^2$ ; for the short section (3) with only 105 points  $\bar{y} = 0\cdot18$ ,  $\Sigma \Delta^2 = 343\cdot5$  and  $\overline{\Delta^2} = 3\cdot27 \text{ mm}^2$ .

\* Fig. I (*d*), Phil. Mag. l. p. 630 (1925).

† Compare fig. 1 (*d*) *loc. cit.*

‡ The last bit of the curve was left out because its mean course there shows an upward deflexion, easily visible in the enlargement, and probably due to some external disturbance.

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For all three sections together we have  $\Sigma \Delta^2 = 2646.2 \text{ mm}^2$ ,  
 $\overline{\Delta^2} = \frac{\Sigma \Delta^2}{685} = 3.86 \text{ mm}^2$ , and thus the mean fluctuation

$$\overline{\Delta} = \sqrt{\overline{\Delta^2}} = 1.97 \text{ mm.}$$

The great deviation on Moll's and Burger's curve, provoked by a potential difference of  $10 \times 10^{-8}$  volt, possessed on the enlarged curve a (mean) ordinate  $y = 213.5 \text{ mm.}$ ; the deviation of  $1.97 \text{ mm.}$  thus corresponds to

$$\frac{1.97}{213.5} \cdot 10^{-7} = 9.22 \times 10^{-10} \text{ volt,}$$

or  $\overline{\delta v'}_{\text{observed}} = 9.22 \times 10^{-10} \text{ volt.}$

We will now compare this value with that calculated by formula (10). This calculation will, of course, be somewhat uncertain, as only approximate statements as to the value of  $R'$  and  $T_0$  are given: "this galvanometer has a time of indication of less than two seconds, its resistance is about 50 ohms" (on p. 629 of the quoted paper). It is probable, both from Dr. Moll's earlier description of the galvanometer\*, and from the published curves, that the galvanometer was used with critical damping; in this case a provoked deviation will reach its end-value to within  $\frac{1}{2}$  per cent. in a time  $= 1.18 T_0$ . Supposing this to be the meaning of the "time of indication" and putting it  $= 1.9 \text{ sec.}^\dagger$ , we get  $T_0 = 1.6 \text{ sec.}$  Assuming further, that the external resistance in the circuit was small, we may put  $R' = 50$ , and thus obtain

$$\overline{\delta v'}_{\text{calc.}} = 1.12 \times 10^{-10} \sqrt{\frac{50}{1.6}} = 6.3 \times 10^{-10} \text{ volt.}$$

This being about two-thirds of  $\overline{\delta v'}_{\text{obs.}}$ , it seems fairly sure that the observed fluctuations in the main were Brownian fluctuations of the primary galvanometer, and only to some small extent due to external perturbations, perhaps micro-seismic ones such as supposed by Moll and Burger  $\ddagger$ . This fact demonstrates very clearly what an admirable stability and freedom from disturbances the constructors have been able to give both to the galvanometer and to the thermo-relay, their combination approaching the theoretical limit of a galvanometer's sensibility.

Physical Laboratory of the University.  
 Stockholm, October, 1925.

\* Proc. Phys. Soc. xxxv. p. 253 (1923).

$\dagger$  The time of indication should be *less* than two sec.

$\ddagger$  On the published curve (d), enlarged, there is scarcely to be found any support for the assumption of a regular *period* of the fluctuations.

LXXIV. *The Efficiency of  $\beta$ -ray Recoil of Radium C from Radium B.* By A. W. BARTON, M.A., B.Sc., Trinity College, Cambridge\*.

*Introductory.*

**E**XPERIMENTS on the  $\beta$ -ray recoil of Radium C from Radium B have previously been performed by Russ and Makower† and Muszkat‡. The former obtained efficiencies of about 0.1 per cent. from a surface of Radium B obtained by exposing a platinum disk to Radium Emanation in the usual way, and the latter using a surface of Radium B prepared by distillation in a vacuum claimed to have obtained values up to 50 per cent.

Recently Jacobsen§ has carried out a determination of the half-period of Radium C' by a method which depends for its success on obtaining an efficient  $\beta$ -ray recoil. In repeating this method with certain modifications, it was thought desirable first of all to investigate thoroughly the phenomenon of  $\beta$ -ray recoil, and the present experiments were performed with that aim in view. Although the conditions were similar the value of the efficiency obtained is considerably lower than that claimed by Muszkat, but as will be shown later it seems to be theoretically reasonable, and moreover an explanation is put forward to account for the discrepancy between the results of these experiments and those obtained by Muszkat.

*A Discussion of the Conditions necessary for an Efficient  $\beta$ -ray Recoil.*

When an atom of Radium B disintegrates emitting an electron the residual atom Radium C receives a velocity in the opposite direction. Taking  $1.7 \times 10^{10}$  cm. per sec. as a mean value of the velocity of the electron, that of the Radium C atom, the recoil atom, is  $4.4 \times 10^4$  cm. per sec., the corresponding energy being 0.4 volt. From Blackett's || work on the range of recoil atoms produced by impact with  $\alpha$ -particles, the range of these Radium C atoms can be estimated to be between  $10^{-6}$  cm. and  $10^{-8}$  cm. of air at atmospheric pressure. Obstructions of this order of thickness in the form of surface films of gas and tarnishing are almost certain to be present on the plate on which the Radium B,

\* Communicated by Professor Sir E. Rutherford, P.R.S.

† Phil. Mag. xix. p. 100 (1910).

‡ Phil. Mag. xxxix. p. 690 (1920).

§ Phil. Mag. xlvii. p. 23 (1924).

|| Proc. Roy. Soc. A, ciii. p. 62 (1923).

the parent atom, is deposited say by exposure to emanation, and would consequently prevent the recoil atoms from escaping from it and being collected on a plate near by. It is evident then that special conditions will have to be realized to obtain an efficient  $\beta$ -ray recoil. In discussing these conditions it is not necessary to argue from a theoretical standpoint, since they can be obtained empirically from the results of previous experiments which have a bearing on the problem.

Consider in the first place experiments on  $\alpha$ -ray recoil. Here the energy of recoil is of the order of 100,000 volts, and so whatever conditions are necessary for its detection must be realized in the case of  $\beta$ -ray recoil. Efficiencies up to 50 per cent. can be obtained in any case of  $\alpha$ -ray recoil provided that the parent atom is deposited on a clean well-polished surface. (An efficiency of 100 per cent. is to be taken to mean that the maximum theoretical number of recoil atoms has been collected.) Any tarnishing of the surface causes a considerable decrease in efficiency. But in some experiments by the author on the recoil of Thorium D from Thorium C efficiencies of 100 per cent. were obtained. The Thorium C was first deposited on a nickel wire by von Lerch's method and then distilled in air from this wire on to a polished brass cylinder, from which the recoil atoms were subsequently collected in a vacuum. The first condition to be satisfied, then, to obtain an efficient  $\beta$ -ray recoil is that the surface of the parent atom must be prepared by distilling it on to a polished plate.

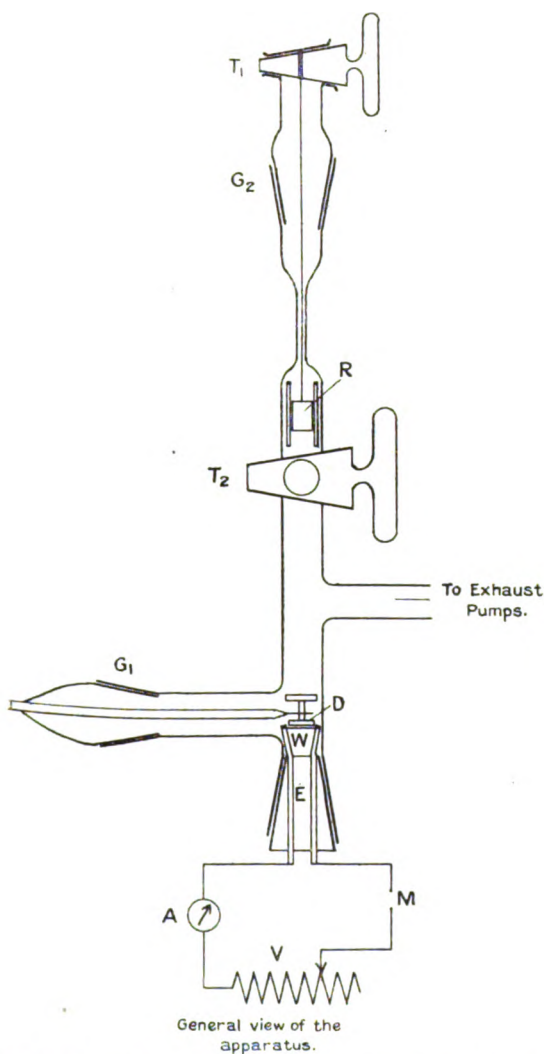
Secondly, consider the experiments on the photoelectric effect with visible radiation where the energy of the electrons is of the same order as that of the  $\beta$ -ray recoil atoms, about one volt. Here the escape of the electrons was greatly impeded unless a "clean" surface was used (a clean surface is one which is prepared in a vacuum and is never afterwards exposed to the atmosphere either before or during use). This will also be true of  $\beta$ -ray recoil atoms, and therefore the second condition to be satisfied to obtain an efficient  $\beta$ -ray recoil is that the parent atom must be prepared in a vacuum and never be exposed to the air before or during recoil.

The simplest way of combining these two conditions in practice is to distil the parent atom from a wire on to a plate close by in a vacuum and to collect the recoil atoms from that plate, which is not exposed to the air until the recoil is stopped. The pressure of the air should be less than  $10^{-3}$  mm. of mercury, since at this pressure the mean free

path of the recoil atoms would be about 7 cm., and so one which has escaped from the surface of the parent atom would be certain to reach a plate a millimetre or so away.

*Description of the Apparatus and Experimental Details.*

Fig. 1.



The arrangement of the apparatus is shown in figs. 1, 2, and 3. Radium Active Deposit is obtained on the platinum

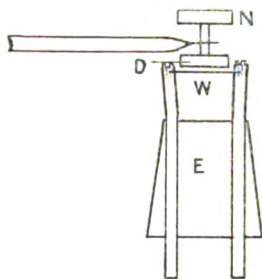


wire W, and is left for 30 mins. to allow the Radium A to decay away, after which it is inserted in the apparatus so that it can be electrically heated to about  $400^{\circ}\text{C}$ ., the heating current being measured by the ammeter A. The temperature, which need not be known accurately, can always be reproduced by using the same heating current.

The apparatus is exhausted by a Gaede Mercury Pump and a Charcoal Tube immersed in liquid air, a liquid-air trap being inserted between the pump and the apparatus to prevent mercury vapour from diffusing into it. A pressure of about  $10^{-4}$  mm. of mercury was obtained, being estimated by a discharge-tube which had been calibrated by a McLeod gauge.

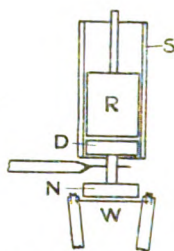
The wire is heated for 60 secs. to about  $400^{\circ}\text{C}$ ., when some of the Radium B and C which distils off condenses on the cold disk D, a brass plate 4 mm. in diameter. The tap  $T_2$  is closed during this distillation to prevent any Radium B and

Fig. 2.



The Cold Disk in Position for the Distillation

Fig. 3.



Cold Disk and Receiver during Recoil.

C reaching the receiver R. It was necessary to use sources as large as 5 mg. of Radium B and C on the platinum wire in order to obtain recoil effects measurable on an  $\alpha$ -ray electroscope, because a temperature of distillation of about  $400^{\circ}\text{C}$ . is the highest that can be used if the efficiency of recoil is not to be greatly decreased, and even then only a small fraction of the amount distilled is collected since the distillation is in a vacuum.

The tap  $T_2$  is then opened, and the cold disk being turned through  $180^{\circ}$  by the ground-glass joint  $G_1$ , the receiver, a brass cylinder 4 mm. in diameter and 5 mm. long, is lowered by the windlass  $T_1$  into the position shown in fig. 3, when a definite fraction of the recoil atoms escaping from the cold disk are collected by it. The screen N and the sleeve S prevent any Radium C recoiling from the Radium B left on the

wire or condensed on the walls of the apparatus from reaching the receiver.

The recoil is allowed to proceed for 30 mins., since it was the average value of the efficiency over 30 mins. which was required for the experiments on the half-period of Radium C'. The receiver is then raised, air is let into the apparatus, and the receiver and cold disk are removed. Their activities were measured by a suitable  $\alpha$ -ray electroscope, that of the cold disk being measured as soon as possible after removal from the apparatus and then again an hour later. The variation of the activity of the receiver was followed carefully for about 50 mins., and from the form of the curve the purity of the deposit could be estimated. Under ideal conditions only Radium C would be obtained showing an exponential decay of half-period 19.5 mins., but in practice a small amount of Radium B is always found. This question of contamination is discussed more fully later, but it can easily be taken into account in the calculation of the efficiency of the recoil. From these measurements of the activities of the cold disk and receiver the efficiency is calculated as shown in the next paragraph.

*Calculation of the Efficiency of Recoil.*

The Efficiency of Recoil,  $\epsilon$ , is defined by the equation

$$\epsilon = \frac{\text{No. of atoms of Radium C escaping from the cold disk by Recoil in any time.}}{\text{Half of Total No. of atoms of Radium C produced by disintegration in that time.}} \quad \dots (1)$$

On this definition the efficiency would be 100 per cent. if the full theoretical number of recoil atoms was obtained.

To calculate the efficiency of recoil from the above measurements, we proceed as follows:—

Let  $B$  = No. of Radium B atoms on the cold disk at any time  $t$ ,

$C$  = No. of Radium C atoms on the receiver at any time  $t$ ,

$C_\tau$  = No. of Radium C atoms on the receiver at time  $\tau$ ,

$\lambda_B, \lambda_C$  = Radio-active constants of Radium B and C respectively,

$\omega$  = Average solid angle subtended by the receiver over the cold disk ( $4 \times 2\pi$  in these experiments),

$\tau$  = Time of duration of recoil.

Then at any time  $t$ ,  $\frac{1}{2} \epsilon B$  atoms of Radium B are effective in producing Radium C atoms which escape from the cold disk. Also at the beginning of the recoil,  $t=0$ ,  $B=B_0$ ,  $C=0$ . A simple application of the laws of radio-active decay leads to the equation

$$C_r = \frac{\omega}{4\pi} \cdot \frac{\lambda_B}{\lambda_B - \lambda_C} \cdot \epsilon B_0 (e^{-\lambda_C r} - e^{-\lambda_B r}). \quad (2)$$

From this equation, knowing  $\omega$ ,  $\tau$ ,  $B_0$ , and  $C_r$ ,  $\epsilon$  can be calculated.

$B_0$  is obtained from the measurements of the activity of the cold disk in the following way :

Let  $B$  = No. of atoms of Radium B on cold disk at any time  $t$ ,

$C_1$  = No. of atoms of Radium C on cold disk at any time  $t$ .

At  $t=0$ , the beginning of the recoil,  $B=B_0$ ,  $C_1=C_0$ . Then,  $B=B_0 e^{-\lambda_B t}$ ,

$$C_1 e^{\lambda_C t} = -\frac{\lambda_B}{\lambda_B - \lambda_C} \cdot B_0 e^{-(\lambda_B - \lambda_C)t} + k,$$

where  $k$  is a constant.

From the initial condition at  $t=0$ ,  $C=C_0$ , we have

$$C_1 = \frac{\lambda_B B_0}{\lambda_B - \lambda_C} \{e^{-\lambda_C t} - e^{-\lambda_B t}\} + C_0 e^{-\lambda_C t}. \quad (3)$$

Now the measured activity of the cold disk is proportional to  $C_1$ , since the ionizing effect of the  $\beta$ -rays from Radium B is negligible compared with that of the  $\alpha$ -rays from Radium C. Thus, by measuring the activity of the cold disk at two times  $t_1$  and  $t_2$ , we obtain from (3) two equations from which the two unknowns  $B_0$  and  $C_0$  can be calculated. In this investigation no account has been taken of the disturbing effect of the recoil on the decay, since with the small efficiencies obtained in these experiments this was found to be negligible.

$C_r$  is obtained by extrapolating the measured activity of the receiver to the time corresponding to the end of the recoil. In addition, it is most important to estimate the purity of the activity on the receiver for two reasons. Firstly, the only reliable criterion that the Radium C on the receiver is due to recoil is its purity. For if it is

accompanied by any appreciable quantity of Radium B (25 per cent. or more), then it is not certain that any of the Radium C present is due to recoil, for whatever caused the Radium B to reach the receiver (and it could not be  $\beta$ -ray recoil) might also have caused the Radium C to reach it also. Secondly, if a small amount (less than 10 per cent.) of Radium B is present, a correction must be applied to allow for the Radium C produced by it, it being certain that the rest of the Radium C present is due to recoil. This was found to be negligible in the final conditions used in the experiments, but initially a considerable amount of Radium B was always found on the receiver due to "contamination," a phenomenon well known to those working in radio-activity. If an apparatus containing a source of some few milligrammes strength is exhausted, it is found that after a few minutes minute traces of the radio-active matter on the source have spread throughout the apparatus and have condensed all over the walls. To this effect is given the name contamination. The way in which it affects the present experiments is as follows. The wire W (fig. 3) is the source from which traces of radio-active matter spread throughout the apparatus, some of it condensing on the receiver R. As the amount of Radium B on the cold disk is only about  $\frac{1}{1000}$  of that on the wire, the amount of Radium C on the receiver due to contamination may easily be of the same order as that due to recoil. The presence of contamination was first discovered by testing the activity of the back of the receiver, which was found to be as great as that of the front. It is impossible to eliminate the effect, but it was found possible to get a strong enough source of Radium B on the cold disk from a parent source of given strength so as to render its effect negligible by adjusting it (the cold disk) to be as close as possible to wire W ( $\frac{1}{2}$  mm.) and by increasing the time of distillation to 1 min. Under these conditions the percentage of Radium C in the activity on the receiver was always greater than 90 per cent., and in an experiment performed solely to test this point, the activity on the receiver decayed exponentially for 80 mins. with a half-period of 20.1 mins. corresponding to 95 per cent. of Radium C. From these results it is certain that the Radium C on the receiver is due to recoil and not to spurious effects such as contamination; but as it is impossible to eliminate completely the latter effects, the values of the efficiency given below should be looked upon as upper limits.

*Results.*

The maximum value of the efficiency of recoil obtained in these experiments was 6 per cent. The efficiency varied considerably in a way which cannot be controlled, but it was always possible to obtain 2 per cent.

The efficiency of recoil from a surface prepared as above and exposed to air for about 30 secs. was also determined, a knowledge of this being required in connexion with the work on Radium C'. The values obtained lay between 1.5 per cent. and 3 per cent. It is evident that even in this short time the "cleanness" of the surface of Radium B is impaired, thus impeding the recoil, which is just what would be expected.

One other interesting fact has emerged in the course of this work. That is, that at about 400° C. in a vacuum Radium C is more volatile than Radium B. This is in striking contrast to the volatility at atmospheric pressure, for at 600° C. Radium B distils readily, Radium C hardly at all. The difference might be due to the fact that the Radium B and C are in different states of chemical combination in air and in a vacuum.

*Modification of the above Method.*

Since in the above method only very small sources of Radium B are obtained, which are quite useless for the experiments on Radium C', the following procedure was tried in the hope of getting good efficiencies but a much stronger source. The platinum wire, on which the active deposit is obtained, is inserted in the apparatus and heated in a vacuum as before. Now the temperature to which the wire is heated is adjusted so that the film of gas and other surface impurities which impede recoil are driven off (together with a little active deposit). But, on the other hand, the lowest temperature which suffices for this purpose must be used, since the heating will tend to drive some of the active deposit into the wire and so impede the recoil. The source prepared in this way will be about 1000 times as strong as that obtained by the method described above, and its surface may be equally favourable to recoil since it should approximate to a "clean" surface.

The efficiency of recoil from such a surface was measured, a few necessary modifications in the apparatus being made. The mean value obtained was 2 per cent., which compares very favourably with that obtained by the first method.

*Discussion of Results.*

The chief point of interest in this work is the low efficiencies obtained (6 per cent.) compared with those obtainable in the case of  $\alpha$ -ray recoil (50–100 per cent.). It is not to be expected that such high efficiencies would be obtained for  $\beta$ -ray disintegration owing to the small energy of recoil, but such a large difference is rather surprising at first sight.

The following considerations may explain this difference. Firstly, the electron which causes the Radium C atom to recoil is emitted from the nucleus. Assuming that the continuous background of  $\beta$ -ray spectra is due to electrons from the nucleus, their velocity varies continuously over a wide range,  $0.93 \times 10^{10}$  cm. per sec. to  $2.4 \times 10^{10}$  cm. per sec. in the case of Radium B, the velocity of the recoil atoms varying from  $2.4 \times 10^4$  cm. per sec. to  $6.2 \times 10^4$  cm. per sec. and the corresponding energies being 0.1 volt and 0.6 volt. Further, these recoil velocities also correspond to temperatures of  $500^\circ$  A. and  $3400^\circ$  A. respectively. The lower temperature is much less than that required to volatilize Radium C in a vacuum, and it appears probable that an atom of Radium C with such a velocity could not escape from the surface, simply because it cannot overcome the surface forces of attraction. Consequently a certain proportion of the Radium C atoms will never escape from the Radium B surface however favourable the conditions. How great this proportion is depends upon the distribution of the number of recoil atoms (and so electrons) over the range of velocities in question and on the velocity at which escape sets in. From the work of Chadwick and Ellis \* the number of electrons rises about uniformly from the minimum velocity, reaching a maximum at about  $1.7 \times 10^{10}$  cm. per sec. and falling uniformly to zero at the maximum velocity. Assuming, as is probable, that only those atoms of Radium C with a velocity greater than  $5 \times 10^4$  cm. per sec. can escape from the surface of the parent atom and be collected, it follows that more than half of them will never do so. It may be, then, that the small value of the efficiency obtained is due in part or entirely to the distribution of the velocity of the recoil atoms over a considerable range. Secondly, the diffusion of the parent atom into the plate on which it is deposited may also cause a decrease of efficiency with time in the case of a recoil as weak as this one. Such a decrease was found by Muszkat and would, assuming her results, make

\* Proc. Camb. Phil. Soc. xxi. p. 274 (1923).

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the average efficiency over half-an-hour about one half of the initial value.

There still remains for discussion the divergence between the value of the efficiency obtained in these experiments and those due to Muszkat. Assuming that the efficiency falls to half its initial value in 20 minutes as claimed by Muszkat, then the average efficiency over 30 minutes for a polished brass cold disk in her experiments would be 18 per cent., whereas in the present experiments only 6 per cent. was obtained. There is one factor which may explain the difference, namely contamination. She makes no mention of it in her work, and her apparatus is just as liable to it as the one described above. As she does not give the percentage purity of the Radium C obtained on the receiver, the extent to which contamination actually influenced her results cannot be estimated, but it is quite possible that this explains the difference, since values of the same order as she gives were obtained in these experiments until contamination was detected.

#### *Summary.*

An experimental determination of the efficiency of  $\beta$ -ray recoil of Radium C from Radium B is described.

The conditions most favourable to  $\beta$ -ray recoil are discussed, and to satisfy them a specially prepared surface of Radium B was used. This was obtained by distilling it from a platinum wire on to a polished brass disk, called the cold disk, in a vacuum. The recoil is then performed directly from this "clean" surface.

When the conditions had been so adjusted that contamination was negligible, the maximum efficiency obtained was 6 per cent.

A modification of the above method is described in which the sources of Radium B obtained are about 1000 times as strong as those obtained by the previous method. The efficiency obtained by this method was about 2 per cent.

It is suggested that the range of velocities of the electrons causing the recoil may be such that more than half of the recoil atoms may not have sufficient energy to escape from even a "clean" surface. This may account for the very low efficiencies obtained.

It is probable that the high value (50 per cent.) obtained by Muszkat was due to the fact that no allowance was made for contamination in her experiments.

I should like in conclusion to express my sincere thanks to Sir Ernest Rutherford, P.R.S., for suggesting this problem and for his advice and encouragement while it was being carried out, and to Mr. G. A. R. Crowe for the preparation of the Radium Active Deposit. I am indebted to the Department of Scientific and Industrial Research for a Maintenance Grant which enabled this work to be carried out.

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LXXV. *The Statistical Mechanics of Assemblies of Ionized Atoms and Electrons.* By R. H. FOWLER\*.

§ 1. *INTRODUCTION.*—In a series of papers Prof. Darwin and the present writer have applied statistical mechanics systematically to assemblies of isolated systems, and in the last of the series have included imperfect gases†. The main object of this last extension was an attack on the properties of matter at the temperatures and densities occurring in stars. For this purpose the theory must be formulated in terms of electrons and positive nuclei, rather than in terms of the atoms and molecules of chemistry. This is easy enough, and, provided that an approach to a correct theory of assemblies of ionized atoms and electrons is possible by such refinements on the theory for perfect gases, little would remain to be done here beyond forming a descriptive catalogue of atomic constants (weights and energies) and constructing the characteristic function.

The outstanding difficulty of the desired theory lies in the well-known question of the convergence of the partition functions (*Zustandsumme*) for the stationary states of excited atoms. A simple treatment of this question has recently been suggested by Urey‡ and Fermi§, rendering such an approach at least formally possible. On reading Urey's paper I attempted to develop his idea by generalizing it for assemblies of any sorts of atoms and ions, and electrons, with a more exact analysis of the necessary hypotheses. I came to regard a certain variant of this theory as physically preferable, though no form seemed completely convincing. This variant is described below, and compared with the original. In default of greater certainty, and in

\* Communicated by the Author.

† Fowler, Proc. Camb. Phil. Soc. xxii. p. 861 (1925), with references to the earlier papers.

‡ Urey, Astrophys. Journ. lix. p. 1 (1924).

§ Fermi, Zeit. für Phys. xxvi. p. 54 (1924).



the belief that the differences between these and the true theory would prove to be of minor practical importance, a particular form of the theory was selected, and an extensive series of calculations for stellar interiors carried out by Mr. Guggenheim. These have since been published \*.

It has been pointed out by Planck †, however, that the theory of Fermi (and its variants) is somewhat artificial, in that it ought to be possible to derive the proper form for the partition function directly and solely from the phase integral of Gibbs (with suitable quantum theory modifications). This position is of course undeniable, and Planck has given a treatment of the phase integral in this sense, based on a certain assumption. It will be necessary to examine Planck's discussion in greater detail here. The arbitrary nature of the simplifying assumption he uses becomes clear in the consideration of wider cases than he treats. His theory when generalized leads to results of very much the same form as that of Urey and Fermi. It has the real logical advantage of being directly based on the phase integral, but the arbitrary simplification it contains leaves it, I believe, almost as far from the real truth.

In spite of these admitted weaknesses, however, all forms of the theory hitherto proposed converge to give much the same results. They may therefore perhaps be accepted with some confidence for hydrogen-like atoms with one electron, for which they have been explicitly developed. They have, however, been applied by Mr. Guggenheim and myself to atoms with more electrons. We assumed in so doing that the series of stationary states of the atom or atomic ion could always be taken to be the series of stationary states revealed by the "optical" spectrum of the atom of the same structure, which can in general be referred to series of stationary states in which one or perhaps two electrons are in excited (non-normal) orbits. The existence of other possible stationary states, as shown by the X-ray levels, was of course recognized, but in the absence of an adequate basis for the construction of the whole aggregate they were omitted. The recent work, however, of Stoner ‡, Pauli §, and Heisenberg ||, amplified by Hund ¶, makes it possible to formulate this aggregate,

\* Fowler & Guggenheim, *Monthly Notices R.A.S.* lxxxv. p. 939 (1925).

† Planck, *Ann. der Phys.* lxxv. p. 673 (1924, Dec.).

‡ Stoner, *Phil. Mag.* xlviii. p. 719 (1924).

§ Pauli, *Zeit. für Phys.* xxxi. p. 765 (1925).

|| Heisenberg, *Zeit. für Phys.* xxxii. p. 841 (1925).

¶ Hund, *Zeit. für Phys.* xxxiii. p. 345 (1925).

it may be crudely but at least with some show of confidence. I am inclined to believe that this is the correct basis for calculation. It makes no difference of course for low temperature, less than  $20,000^{\circ}$  or  $30,000^{\circ}$ . But for the high temperatures of stellar interiors the results are interesting and sometimes significantly different in certain respects from the simpler theory of one excited electron.

The substance of this paper formed certain chapters of an essay submitted for the Adams Prize of 1923-24 on Statistical Mechanics with special reference to the properties of matter at stellar temperatures. This paper, however, is the result of a complete revision of the earlier work.

§ 2. *Summary of the paper.*—The contents of this paper are therefore as follows :—

In § 3 we give a formal specification of atomic dissociation theory in terms of atomic ions and free electrons on the general basis provided by statistical mechanics for assemblies of isolated systems\*. In the first instance it has been assumed that the constituents behave as perfect gases with formal expressions  $u(T)$  for their series of stationary states. This has then been amplified to include the electrostatic term of Debye and Hückel †, and corrections for the volume of each ion according to the theory (generalized) of van der Waals.

In § 4 we specify the *energies* ( $\chi_r^z$ ), of the various atoms ( $Z$ ) in the various stationary states ( $s$ ) of their various stages of ionization ( $r$ ), and in § 5 the *weights* ( $\varpi_r^z$ ), of these states. These are required unaltered in any form of the theory.

It is becoming increasingly necessary to form a standard specification of these weights for general statistical use, which it is hoped this section will provide.

In § 6 we investigate the form of  $u(T)$  according to the generalized theory of Urey and Fermi, and in § 7 the variant on which numerical calculations for stars have already been made. We show further how the  $u(T)$  of these theories can be approximately summed for atoms with one or any other number of excited electrons. These summations are extended in § 8.

In § 9 Planck's suggestion is investigated and generalized, and the resulting form of  $u(T)$  established, and in § 10 the various theories are collated. Actual applications of the theories to stellar or other problems are not undertaken here.

\* Fowler, *loc. cit.*

† Debye & Hückel, *Phys. Zeit.* xxiv. pp. 185, 305 (1923).

§ 3. *The fundamental formulæ.*—We shall discuss the average state of an assembly so hot that we no longer require to recognize the existence of molecules. They can easily be included if necessary. We proceed to construct formally the characteristic function  $\Psi^*$ .

As a suitable notation let

$M_0^z$  be the (average) number of neutral atoms of atomic number  $Z$  in a volume  $V$ ;

$M_r^z$  be the (average) number of such atoms  $r$ -times ionized;

$N$  be the (average) number of free electrons.

In general atoms  $r$ -times ionized must be defined to mean nuclei accompanied by  $Z-r$  electrons, each of which has insufficient energy to effect an escape. That each single electron bound to a nucleus has a definite energy may be regarded as a postulate of the Quantum theory demanded by the facts of spectroscopy. The most convenient standard state of (conventionally) zero energy is that state of the assembly in which the only constituents are electrons and bare nuclei at rest at infinite separation. The bare nucleus and the electron are assumed structureless, and will have partition functions  $VF_z^z(T)$  and  $VG(T)$  of the usual form (p. 863). We shall use  $m$  for the mass of the electron and  $m^z$  for the bare nucleus  $Z$ . It will never be necessary to distinguish between  $m^z$  and  $m^e + rm$  ( $r \leq z$ ).

Consider next the normal state of each atomic ion. Let the successive ionization energies of the atom  $Z$  be  $\chi_0^e, \chi_1^e, \dots, \chi_{z-1}^z$  and the weights of their normal states  $\varpi_r^z$ . Then, for the  $r$ -times ionized atom the partition function  $VF_r^z(T)$  is given by

$$F_r^z(T) = \frac{(2\pi m^z kT)^{\frac{3}{2}}}{h^3} \varpi_r^z e^{\{\chi_r^z + \dots + \chi_{z-1}^z\}/kT} \dots \quad (1)$$

Each ion will in addition possess a number of excited states of greater energy content, which, on the perfect gas basis, will cause  $\varpi_r^z$  to be formally replaced by the factor  $b_r^z(T)$ , where

$$b_r^z(T) = \sum_{s=0} (\varpi_r^e)_s e^{-\{\chi_r^e - (\chi_r^e)_s\}/kT} \dots \quad (2)$$

The state  $s=0$  is the normal state of least energy and we continue to write  $\varpi_r^e$  and  $\chi_r^e$  instead of  $(\varpi_r^e)_0$  and  $(\chi_r^e)_0$ . The energy of excitation is  $\chi_r^e - (\chi_r^e)_s$ , so that  $(\chi_r^e)_s$  corresponds to a spectral term (the  $s$ th) of the  $r$ -times ionized atom  $Z$ .

\* Fowler, *loc. cit.* p. 863. Further references in this § to the same paper will be incorporated in the text with a page reference only.

When allowance is made for excluded volumes  $b(T)$  is replaced by  $u(T)$ , where (p. 875)

$$u_r^z(T) = \sum_{s=0} (\varpi_r^z)_s \exp \left[ -\{\chi_r^z - (\chi_r^z)_s\}/kT - \{N(v_r^z)_{s,\epsilon} + \sum_{\beta} M_{\beta}(v_r^z)_{s,\beta}\}/V \right]. \quad (3)$$

In equation (3) the average excluded volume for interaction with an electron is  $(v_r^z)_{s,\epsilon}$  and with an atomic ion  $\beta$   $(v_r^z)_{s,\beta}$ . The summation  $\sum_{\beta}$  is taken over all atomic types  $(r', s', z')$ . The complete form for  $\Psi$  is then (p. 875)

$$\Psi/k = N \left( \log \frac{VG}{N} + 1 \right) + \sum_{r,z} M_r^z \left( \log \frac{VF_r^z}{M_r^z} + 1 \right) + \frac{1}{V} \sum_{\alpha,\beta} \frac{M_{\alpha} M_{\beta} v_{\alpha\beta}}{\sigma_{\alpha\beta}}. \quad (4)$$

For completeness we repeat \*

$$F_r^z = \frac{(2\pi m^z kT)^{\frac{3}{2}}}{h^3} u_r^z(T) e^{\{\chi_r^z + \dots + \chi_{z-1}^z\}/kT}, \quad G = \frac{(2\pi m kT)^{\frac{3}{2}}}{h^3}. \quad (5)$$

$\sum_{\alpha,\beta}$  is a summation over all pairs of types of massive ions and  $\sigma_{\alpha\beta}=1$  ( $\alpha \neq \beta$ ),  $\sigma_{\alpha\alpha}=2$ . It is a further consequence of equations (3), (4), and (5) that (p. 876)

$$\frac{\partial \Psi}{\partial M_{\alpha}} \equiv \frac{\partial \Psi}{\partial (M_r^z)_s} = 0 \quad (\text{all } r, s, z), \quad (6)$$

so that in any variation of  $N$  or  $M_r^z$  no explicit variation of any  $M_{\alpha}$  need be made. The excluded volume corrections, when not small, are only qualitatively correct (p. 876). Further (p. 875)

$$\frac{(M_r^z)_s}{(\varpi_r^z)_s \exp \left[ -\{\chi_r^z - (\chi_r^z)_s\}/kT - \{N(v_r^z)_{s,\epsilon} + \sum_{\beta} M_{\beta}(v_r^z)_{s,\beta}\}/V \right]} = \frac{M_r^z}{u_r^z(T)}. \quad (7)$$

To the value of  $\Psi/k$  given by (5) we must add (a) the

\* (Added in proof).—In the theory of Goudsmit and Uhlenbeck (see footnote to § 5)  $G$  is greater by a factor 2.

contribution of radiation in the enclosure (p. 863)\*, and (b) the term arising from the electrostatic charges on the massive ions and free electrons. The radiative term is properly additive. Electrostatic and excluded volume effects really interact and should be introduced together, which could probably be done by a more extensive investigation. We shall, however, be content here with the simplest form for point ions†. The complete form for  $\Psi$  is therefore

$$\Psi/k = N \left( \log \frac{VG}{N} + 1 \right) + \sum_{r,z} M_r^z \left\{ \log \frac{VF_r^z}{M_r^z} + 1 \right\} \\ + \frac{1}{V} \sum_{\alpha,\beta} \frac{M_\alpha M_\beta v_{\alpha\beta}}{\sigma_{\alpha\beta}} + \frac{8\pi^5 k^3 VT^3}{45c^3 h^3} + \frac{2\sqrt{\pi}\epsilon^2}{3V^{\frac{1}{2}}(kT)^{\frac{3}{2}}} \{N + \sum_{r,z} r^2 M_r^z\}^{\frac{3}{2}}. \quad (8)$$

In conjunction with (3) and (5), (8) determines all the equilibrium properties of the assembly.

3.1. *Dissociative Equilibrium.* Submit  $\Psi$  to the variation

$$\delta M_r^z = -\eta; \quad \delta N = \delta M_{r+1}^z = \eta;$$

for which  $\delta\Psi=0$ . The  $(M_r^z)_s$  need not be varied explicitly. By combining (3) and (7) we can show that

$$\sum_{r,z} \frac{M_r^z}{u_r^z} \frac{\partial u_r^z}{\partial N} = -\frac{1}{V} \sum_{\beta} M_{\beta} v_{\beta,z}. \quad (9)$$

With the help of (5) and (9) we find

$$\frac{NM_{r+1}^z}{VM_r^z} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{u_{r+1}^z(T)}{u_r^z(T)} \exp \left[ -\frac{\chi_r^z}{kT} - \frac{1}{V} \sum_{\beta} M_{\beta} v_{\beta,z} \right. \\ \left. + \frac{2\sqrt{\pi}\epsilon^2(r+1)}{V^{\frac{1}{2}}(kT)^{\frac{3}{2}}} \{N + \sum_{r,z} r^2 M_r^z\}^{\frac{1}{2}} \right]. \quad (10)$$

This is the generalized form of the law of mass-action, ionic volumes and charges being taken into account. It is

\* For the radiation partition function, see *e.g.* Proc. Camb. Phil. Soc. xxi. p. 262 (1922).

† The validity of the numerical coefficient of the electrostatic term is more than doubtful. Eddington (M. N. vol. lxxvi. p. 2 (1925)) has pointed out a correction which appears to reduce it by a factor about  $\frac{1}{3}$ . At the same time the weak point in the Debye-Hückel theory (Fowler, *loc. cit.* p. 881) may be becoming important, and it may be preferable to trust to Milner's results (Phil. Mag. xxiii. p. 551 (1912), and xxv. p. 742 (1913)). An extended re-examination is desirable.

more commonly expressed in terms of  $p_e$ , the partial pressure of the electrons, calculated as a perfect gas, when it takes the form

$$\frac{M_{r+1}^z}{M_r^z} p_e = \frac{(2\pi m)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{h^3} \frac{u_{r+1}^z(T)}{u_r^z(T)} \exp \left[ -\frac{\chi_r^z}{kT} - J + L \right], \quad (11)$$

say, where  $J$  is the extra volume term and  $L$  the extra charge term. Combined with

$$\Sigma_r M_r^z = M^z \text{ (all } z); \quad \Sigma_{r,z} r M_r^z = N, \quad . \quad . \quad (12)$$

equation (10) or (11) determines the degree of ionization in the equilibrium state.

3.2. *The pressure,  $T\partial\Psi/\partial V$ .* We find

$$\begin{aligned} p = kT \left[ \frac{N + \Sigma_{r,z} M_r^z}{V} + \frac{8\pi^5 k^3 T^3}{45 c^3 h^3} + \frac{1}{V^2} \left\{ N \Sigma_{\beta} M_{\beta} v_{\beta}, e \right. \right. \\ \left. \left. + \Sigma_{\alpha, \beta} \frac{M_{\alpha} M_{\beta} v_{\alpha\beta}}{\sigma_{\alpha\beta}} \right\} - \frac{\sqrt{\pi} \epsilon^3}{3(VkT)^{\frac{3}{2}}} \left\{ N + \Sigma_{r,z} r^3 M_r^z \right\}^{\frac{3}{2}} \right], \\ = p_e + p_a + p_r + p_{c_1} + p_{c_2}, \quad . \quad . \quad (13) \end{aligned}$$

say, where  $p_a$  is the partial pressure of the massive ions,  $p_r$  the radiation pressure, and  $p_{c_1}$ ,  $p_{c_2}$  the correcting volume and charge terms respectively.

3.3. *The entropy.* This can be calculated directly as  $\Psi + T\partial\Psi/\partial T$ . The  $(V, T)$ -adiabatics of the assembly are then given directly by  $S = \text{const.}$  The resulting general expression is complicated, and to obtain the  $(P, V)$ -equation of the adiabatics, which is usually required, it is somewhat simpler to proceed by calculating directly the ratio of the specific heats.

§ 4. *The ionization energies  $\chi_r^z$  and the energies  $(\chi_r^z)_s$  of the stationary states.*—To use the formulæ of § 3 we must, strictly speaking, know  $(\chi_r^z)_s$  for all  $r, s, z$ , that is all the spectral terms (in the widest sense) of all atoms in all stages of ionization. Such knowledge will perhaps never be available, but practical requirements are less exacting, and differ for applications to the insides and outsides of stars. For outsides of stars, to study theoretically the behaviour of a given absorption line, we require to know little more than the  $(\chi_r^z)_s$  of the state from which the absorption line arises,

and the  $\chi_r^z$  for the normal atom or ion, to the optical spectrum of which the line belongs. We are seldom required in such problems to consider series of stationary states in which more than one excited electron is concerned—besides the series for one electron at most a very few stationary states of the other electrons are concerned. The necessary  $(\chi_r^z)_s$  and  $\chi_r^z$  are known exactly as soon as the spectrum is analysed.

For the insides of stars a representative selection of elements should be sufficient. The calculations referred to have been done with O, Fe, and Ag. Here the  $(\chi_r^z)_s$  are merely important in the calculation of the  $u_r^z(T)$ , in which either only the states of high excitation are relevant or else the normal state (or nearly normal states) alone. In states of high excitation of *one* electron all atoms become nearly hydrogen-like, and, arranged in suitable sequences, the  $(\chi_r^z)_s$  take Rydberg's approximate form  $(r+1)^2 R^* hc / (n-\mu)^2$ . [ $R^*$  is Rydberg's constant, and  $c$  is the velocity of light.] It is generally sufficiently accurate to ignore the constant  $\mu$ . Approximations for more than one excited electron would be less simple, but it will appear that *zero* is a sufficiently good approximation. Only the  $\chi_r^z$  are left and these are wanted accurately. It must be remembered that these are the energies required to remove the electrons one after the other, leaving a normal ion at each stage. They are *not* the energies of the X-ray levels, and must always exceed these owing to the diminished screening. They may be greater by a factor as great as 5 in certain cases, and factors exceeding 2 are common.

Few values of  $\chi_r^z$  are known by direct observation, but it has recently been shown by Hartree† that the majority of them can be fixed with some security by theoretical extrapolations based on our knowledge (after Bohr's theory) of the structure of atoms and spectra. The most important can be best fixed thus. Hartree has constructed tables for O, Fe, and Ag, and tables for other elements can be filled in by the same methods.

In constructing and applying these tables, a definite assumption must be made as to the normal order in which the orbits are filled up in normal ions. The order of filling up of two specified  $n_k$  orbits is (as is well known) not always the same for all nuclear charges, but is almost certainly always the same for all large enough nuclear

† Hartree, Proc. Camb. Phil. Soc. xxii. p. 464 (1924).

charges. Uncertainties of order thus only affect lightly bound orbits, are accessible to direct observation, and irrelevant in stellar interiors. It seems, however, now possible to be fairly certain of the numbers of electrons in each group or subgroup of the atom, even in the complicated structures of the Fe (and similar) transition elements \*. The order assumed is the following :—

(a) Number of electron in order of capture.	(b) Type $n_k$ of ultimate normal orbit.	(a) Number of electron in order of capture.	(b) Type $n_k$ of ultimate normal orbit.
1	$1_1$	25	$3_3$
2	$1_1$	26	$3_3$
3	$2_1$	27	$3_3$
4	$2_1$	28	$3_3$
5	$2_2$	29	$4_1$
6	$2_2$	30	$4_1$
7	$2_2$	31	$4_2$
8	$2_2$	32	$4_2$
9	$2_2$	33	$4_2$
10	$2_2$	34	$4_2$
11	$3_1$	35	$4_2$
12	$3_1$	36	$4_2$
13	$3_2$	37	$4_3$
14	$3_2$	38	$4_3$
15	$3_2$	39	$4_3$
16	$3_2$	40	$4_3$
17	$3_2$	41	$4_3$
18	$3_2$	42	$4_3$
19 (1)	$3_3$	43	$4_3$
20 (2)	$3_3$	44	$4_3$
21	$3_3$	45	$4_3$
22	$3_3$	46	$4_3$
23	$3_3$	47 (3)	$5_1$
24	$3_3$	48 (3)	$5_1$

(1) For  $Z \geq 21$  (Sc) at least some  $3_3$  orbits must precede  $4_1$ . From Sc to Cu there are (according to Hund) always one or two (usually two)  $4_1$  orbits, the electrons from 19 to  $Z-2$  or  $Z-1$  inclusive being bound in  $3_3$  orbits.

(2) For  $Z \geq 22$  (Ti), after Hund, and so on through this transition group.

(3) For Ag and Cd only. For large enough  $Z$ 's permanent  $4_1$  orbits must begin at 47, but this region will not concern us.

\* The number of electrons in completed sub-groups—2; 2, 2, 4; 2, 2, 4, 4, 6; etc.—are those established by the work of Stoner and Pauli (*loc. cit.*), which were first formulated by Main Smith, 'Chemistry and Atomic Structure,' 1924.



§ 5. *Weights*.—Weights are required for all stages of ionization, due account being taken of the way in which they are to be combined, and of the fact that all electrons are identical. Recent theories, particularly the work of Pauli, enable these specifications to be completed with some confidence. We start by assuming that all electrons in the atom are recognizably different and never interchanged.

All atoms and atomic ions are degenerate quantized systems. Any weight may therefore be supposed to be determined—in conformity with Bohr's postulates—by a study of the Zeeman effect in suitable magnetic fields. A "weak" magnetic field assigns, we believe, to the axis of the atom definite orientations, and the number of such different orientations must by the postulates be taken to be the *relative* weight of the normal degenerate case. Since the atom is being orientated as a whole, it does not follow at once that this is a sufficient analysis.

In the general classification of the simpler spectra, which is valid so long as the atom can be divided into a core and single series electron\*, a term or state is specified by four quantum numbers  $n$ ,  $k$ ,  $j$ , and  $r$ , and denoted  $n_k^r j$ . Of these  $n$  and  $k$  have their familiar meanings of the theory of central orbits, and  $j$  and  $r$  define the moments of momentum of the whole atom and the core. The formal specifications of the spectrum are usually made in terms of numbers  $K$ ,  $J$ , and  $R$  such that  $K = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$  for S, P, D, ... terms,  $R = \frac{1}{2}, 1, \frac{3}{2}, \dots$  for singlets, doublets, triplets, ..., and

$$|K - R| + \frac{1}{2} \leq J \leq K + R - \frac{1}{2}.$$

A very simple rule holds in all such cases. The total number of states into which  $n_k^r j$  splits in a weak field is  $2J$ , and the total number of states into which a whole multiplet  $n_k^r$  splits is  $4RK$  [ $2R(2k-1)$ ]. The numbers  $2J$  and  $4RK$  are the relative weights.

The relative weights so determined must give the right ratios for any two states of the same ion, the closed groups of the core being unaltered, but the question whether the scale is always the same, so that the weights of all Zeeman components of all ions are the same, lies deeper. The recent work of Pauli, however, seems to be able to be presented so

\* Or as one now says, "In scheme I" (Heisenberg, *loc. cit.*).

as to lead logically to a definite conclusion, and there is little doubt that his theory presents one aspect of the truth.

Pauli shows that a large section of spectral facts can be described by assigning to all the electrons in any ion, not members of closed groups, the whole peculiar properties of the single series electron of an alkali. The alkali spectrum is to be described thus:—The core of closed groups of electrons is isotropic without mechanical or magnetic moment. The series electron has an unmechanical duplecity (*Zweideutigkeit*) which gives rise to the (relativity) doublet form of the spectrum and so, for given  $k$ , to  $4K$  stationary states of the outer electron in a magnetic field. These states are specified in terms of four quantum numbers  $n$ ,  $k_1$ ,  $k_2$ , and  $m_1$ , or  $n$ ,  $k_1$ ,  $m_1$ , and  $m_2$ , the latter being the suitable set for strong magnetic fields\*. If we have two such series electrons, we may continue to ascribe to the core and each separate series electron the same alkali-like properties, and we obtain by combination of the  $4K_1$  and  $4K_2$  possible states of the two electrons not only the right number of observed terms, arrangeable in the correct groupings (weights), but also the correct magnetic energies in strong magnetic fields. We get the correct results also for more than two electrons. The argument is carried through for strong fields for which the interactions of the various electrons can be ignored. But owing to the invariance of the weights (or numbers of terms) deductions as to weights and term numbers will hold good in general.

Pauli's presentation of these facts has a valuable element of generality in that it does not directly classify the resulting terms into multiplets, for it is clear that, in complicated cases, more than one such classification may be significant. The spectrum of Ne as classified (i.) in the usual way by Paschen, (ii.) according to the new principles of Heisenberg, is an example of this†. It seems in short to be sufficiently clear that in general an atom containing,

\* For convenience of reference we recall that  $k_1$  is the azimuthal quantum number (ordinarily  $k$ ) defining the mechanical nature of the central orbit, while  $k_2$  not necessarily equal to  $k_1$  defines the relativity effect, and  $m_1$  (or  $m$ ) the component of the atomic moment of momentum parallel to an external magnetic field. For strong fields we drop  $k_2$  and use instead  $m_2$  which specifies directly the extra energy in the magnetic field, and is unmechanically unequal to  $m_1$ .

† Hund, *loc. cit.*

besides closed groups,  $q$  electrons in various  $n_k$  orbits would have

$$2^{2q} K_1 K_2 \dots K_q \dots \dots \dots (14)$$

possible stationary states in a magnetic field. Each of these must naturally be assigned an equal weight\*.

Pauli's theory could not, however, have been applied with such confidence without the beautiful subsidiary principle which he has combined with it, namely that

*It is never possible for an atom to contain two or more electrons for which all four quantum numbers are the same. When one electron is present with given  $n$ ,  $k_1$ ,  $k_2$ ,  $m_1$  (or  $n$ ,  $k_1$ ,  $m_1$ ,  $m_2$ ) that place is "engaged".*

This principle leads at once to the closing of groups and subgroups, in agreement with the specifications of Main Smith and Stoner. It accounts also in a most convincing way for the absence of particular terms—for example, of a deep triplet  $s$ -term in the alkaline earths. The number of electrons required to form a complete subgroup of a given  $k$  is equal to the number of such states,  $4K$ . For  $k=1$  the number is therefore 2. With two such electrons in orbits of the same  $n$  there is only *one* realizable possibility instead of 4, and the triplet  $s$ -term must drop out. This is true in general, and a closed group of  $q$  ( $=4K$ ) equivalent  $n_k$  electrons has its possible states reduced from  $(4K)^q$  to 1. Viewed in this way it is at once obvious that the contribution of any closed group to the weight is always a factor unity. Similar but partial reductions occur when any two or more equivalent electrons are present although no group is thereby closed. We see too that the original assumption that cores of closed groups have always only one position in an external field is not an independent assumption but a natural consequence of Pauli's principle of exclusion. The same principle justifies us further in asserting that we can distinguish between any two electrons in the atom by the values of their four quantum numbers, even when we remove our initial assumption that the electrons themselves are recognizably distinct.

Applying Pauli's theory therefore to every electron in the atom, we can properly and systematically take the relative weight of any possible structure of the given number of elec-

\* We are led of course to the same total number of terms by a repeated use of the branching principle with the successive space quantization of the electrons recently proposed by Heisenberg (*loc. cit.*). This equality of terms is fundamental to simultaneous significance of both pictures.

trons to be  $2J$ , as fixed by the Zeeman effect, whatever the orbits of the electrons and whether or no the closed groups of the core are left untouched or broken up. When we group together all the possible multiplets arising in Heisenberg's theory from  $q$  non-equivalent electrons in given  $(n_1)_{k_1}, (n_2)_{k_2}, \dots$  orbits, the correct relative weight is given by (14) with the reductions indicated.

There remains the question of the "absolute" values of these weights compared to the weight  $dp dq/h$  of an element of classical phase space, or compared to the weights of an atom with a different number of electrons. It has been pointed out by Bohr \* that the number of states of an atom cannot be derived in the ordinary mechanical way from the product of the number of states of an ion and an electron brought into its field. The actual number is practically twice as great as one would thus calculate, in consequence of the duplexity. If we assign (say) unity as the weight of each resolved state in every atom, then the sum of the weights changes discontinuously when a free electron is bound. There is nothing thermodynamically or statistically impossible in this discontinuity, but there is a failure of *the limiting principle*, whereby the quantum theory should tend asymptotically to the classical theory for large quantum numbers. In the case in question, the partition function  $\sum \omega e^{-\chi/kT}$  summed over states of large quantum numbers for  $q$  electrons should tend asymptotically to

$$\frac{1}{h^{3q}} \int e^{-\chi/kT} dp_1 \dots dq_{3q}.$$

It is easily seen that it does not. Suppose we have an atom with  $q$  electrons all in orbits of different principal quantum number  $n$ . Then the total number of stationary states is

$$2^q \left\{ \sum_1^{n_1} (2k_1 - 1) \right\} \left\{ \sum_1^{n_2} (2k_2 - 1) \right\} \dots \left\{ \sum_1^{n_q} (2k_q - 1) \right\} \\ = 2^q n_1^2 \dots n_q^2. \quad (15)$$

But by comparison with the hydrogen weights  $n(n+1)$  (see also § 6) the proper asymptotic form to conserve the limiting principle would lack the factor  $2^q$  which arises from the duplexity. It seems therefore necessary to assert that the unit of weight for any ion of  $q$  electrons is  $1/2^q$ . This does not apply to hydrogen or hydrogen-like ions, and it seems not unreasonable that the hydrogen weights should be disubtle those to be expected from the general rule. In an

\* Bohr, *Ann. der Phys.* lxxi. p. 228 (1923), esp. p. 276.

unmechanical way they have an extra degeneracy due to the failure of the duplexity for a single electron, which cannot materialize in a purely Coulomb field \*.

The foregoing count refers only to the assumption of non-interchangeable electrons. This however is exactly what we require, if, in combining weights for the whole assembly, we multiply as usual the complexions for any particular example of the assembly by

$$\frac{X!}{N!} \frac{\Pi_z (M_z!)}{\Pi_{r,z} (M_{r,z}!)} \dots \dots \dots (16)$$

where  $X$  is the total number of electrons, bound or free. The factor  $X!/N!$  is the total number of permutations of all the electrons in the assembly in which a number  $N$ , unspecified in order, are free. This factor therefore allows completely for all possible permutations of the individual electrons, now no longer regarded as distinguishable, in a single atom. If we choose to regard certain of the electrons as permanently bound, they are then simply omitted from  $X$ , and are no longer counted in the possible permutations in a single atom. The same weights must be used.

In view of the preceding rules and theories we can collect together the leading results:—

- (1) The weight of a single term  $n_k^r$  in any spectrum of any atom with  $s$  electrons in all is  $2J/2^s$ .
- (2) The total weight of any multiplet term  $n_k^r$  in any spectrum of any atom with  $s$  electrons in all is  $4Rk/2^s$ .
- (3)† The total weight of all terms arising from  $q$  series electrons in given  $n_k$  orbits in an atom with  $s$  electrons in all ( $s-q$  in closed groups) is

$$2^q K_1 K_2 \dots K_q / 2^{s-q}.$$

This is subject to reductions when any of the  $q$  series electrons are in orbits of the same  $n$  and  $k$ .

- (4)† The total weight of all terms arising from  $q$ -series electrons in orbits of given principal quantum

\* (Note added in proof).—It seems probable that atomic theory will shortly be rewritten in terms of the spinning electron of Goudsmit and Uhlenbeck ('Nature,' Feb. 20, 1926; *Zeit. für Phys.* vol. xxxv. p. 625 (note)). In this theory the extra factor 2 in the sum of the weights on adding a new electron arises from the structure of the electron, which has always 2 possible orientations and a weight twice that here assigned to it. There is an extra factor 2 in  $G(T)$ , and the unit of weight for any ion of  $q$  electrons is always 1. The equations of dissociative equilibrium of this paper are mercifully unaltered.

† See also the extended form (3, 4) below.

numbers  $n_1, n_2, \dots$  in an atom with  $s$  electrons in all ( $s-q$  in closed groups) is

$$n_1^2 \dots n_q^2 / 2^{s-q}.$$

This is subject to reductions when any of the  $q$ -series electrons are in orbits of the same  $n$ .

- (5) The weight of the  $n$ -quantum orbit in an atom with one electron is  $n(n+1)$ .
- (6) These weights are to be combined together as they stand to form the weight of any complexion of any example of an assembly, the number of examples being given by (16). The weights as given have therefore been calculated with selected electrons in each orbit, no interchanges being allowed.

It is of course unnecessary to retain the  $2^s$  factors in statistical problems involving an atom in only one stage of ionization\*.

It may be useful to tabulate here the weights  $\omega_j^z (= \omega_r^{z+r})$  of the terms of lowest energy for a number of atoms. The "weight" which is most valuable in this connexion may be

Atom.	Number of electrons in closed groups.	$\omega_0^z$ .	Atom.	Number of electrons in closed groups.	$\omega_0^z$ .
1 H	0	2	19	18	$10/2^{19}$
2 He	2	$1/2^2$	20	18	$45/2^{20}$
3 Li	2	$2/2^3$	21	18	$120/2^{21}$
4 Be	4	$1/2^4$	22	18	$183/2^{22}$
5 B	4	$6/2^5$	23	18	$250/2^{23}$
6 C	4	$15/2^6$	24	18	$183/2^{24}$
7 N	4	$20/2^7$	25	18	$120/2^{25}$
8 O	4	$15/2^8$	26	18	$45/2^{26}$
9 F	4	$6/2^9$	27	18	$10/2^{27}$
10 Ne	10	$1/2^{10}$	28	28	$1/2^{28}$
11 Na	10	$2/2^{11}$	29	28	$2/2^{29}$
12 Mg	12	$1/2^{12}$	30	30	$1/2^{30}$
13 Al	12	$6/2^{13}$	31	30	$6/2^{31}$
14 Si	12	$15/2^{14}$	32	30	$15/2^{32}$
15 P	12	$20/2^{15}$	33	30	$20/2^{33}$
16 S	12	$15/2^{16}$	34	30	$15/2^{34}$
17 Cl	12	$6/2^{17}$	35	30	$6/2^{35}$
18 A	18	$1/2^{18}$	36	36	$1/2^{36}$

\* (Note added in proof).—In the theory of Goudsmit and Uhlenbeck these factors  $2^s$  do not occur, and the weight of the  $n$ -quantum orbit in an atom with one electron is  $2n^2$ . Hydrogen-like atoms are no longer apparent exceptions.

taken to be the sum of the weights of all terms in which all the electrons are in orbits of the proper (least possible) values of  $n$  and  $k$ . In the case of atoms after A, 18, we give the values suitable for large core charges, the  $3s$  orbits being next added according to the scheme of § 4. The values for Nos. 3–10, repeated for 11–18 and 29–36, are from Pauli; the values for 19–28 from Hund.

It will be necessary in applications to be able to divide up the electrons in any ion into those in their normal or nearly normal orbits—orbits of normal  $n$  and  $k$ —and those in orbits of high excitation. This division will not necessarily be the same as a division into electrons in closed groups or subgroups and the rest, though these divisions will most frequently agree. The foregoing rules refer explicitly to a division into closed groups and other electrons, but they can easily be reformulated. In rules (3) and (4) above the factor  $1/2^{s-q}$  is really the weight of the atomic core of closed groups. When the core of  $s-q$  electrons is not entirely composed of closed groups, we have merely to substitute the weight  $\varpi_0^{s-q}$  from the foregoing table for  $1/2^{s-q}$ . Rules (3) and (4) then read :

- (3, 4)' The total weight of all terms arising from  $q$  series electrons in orbits of given  $n_k$  (given  $n$ ) in an atom with  $s$  electrons in all is

$$2^q K_1 K_2 \dots K_q \varpi_0^{s-q} \quad (n_1^2 \dots n_q^2 \varpi_0^{s-q}).$$

This is subject to reductions when any of the  $q$  series electrons are in orbits of the same  $n_k$  (same  $n$ ) \*.

§ 6. *The Theory of Urey and Fermi*.—In this theory the atoms and ions are assigned an actual volume equal to that of a sphere whose radius is the semi-axis major of the orbit of the electron. Hitherto it has been formulated for hydrogen only. The formulæ of § 3 are at once applicable, determine  $u$  (T), and lend themselves to generalization. The excluded volumes of equation (3) are then spheres whose radius is the sum of the radii of the two interacting types. In the approximations of Urey and Fermi the radius of the interacting system ( $\beta$ ) is neglected compared to the radius of the  $(r, s, z)$ -ion itself. This will introduce no error at low temperatures in the cases they discuss in which highly

\* (*Added in proof*).—In the theory of Goudsmit and Uhlenbeck these formulæ become  $2^{2q} k_1 k_2 \dots k_q \varpi_0^{s-q}$ ,  $2^q n_1^2 \dots n_q^2 \varpi_0^{s-q}$ .

excited orbits are rare. As a result we obtain from (3) for hydrogen :

$$u(T) = \sum_t t(t+1) \exp \left\{ -\frac{\chi}{kT} \left( 1 - \frac{1}{t^2} \right) - \alpha t^6 \right\}, \quad (17)$$

where

$$\alpha = \frac{4\pi}{3} \frac{N + \sum_{\beta} M_{\beta}}{V} a^3 = \frac{4\pi}{3} \frac{p_e + p_a}{kT} a^3. \quad (18)$$

In (18)  $a$  is the radius of the 1-quantum orbit in hydrogen,  $5.34 \times 10^{-9}$  cm., and  $\chi$  its ionization energy, 13.54 volts. More generally at high temperatures a better approximation to (3) is obviously provided by replacing  $t^6$  by  $(t_0^2 + t^2)^3$ , where  $at_0^2$  is the average radius of all the interacting systems. This improvement will not affect orders of magnitude and we shall not investigate it in detail.

To formulate the theory for any atom with one excited electron we have obviously only to replace  $\alpha t^6$  by  $\alpha n_t^6/(r+1)^3$  and  $t(t+1)$  by  $\varpi_t$ , where  $n_t$  is the effective quantum number and  $\varpi_t$  the weight of the  $t$ th orbit and  $r+1$  is the core charge. For an atom with any number of excited electrons we have presumably to replace  $n_t$  by  $(n_{\max})_t$ , denoting thereby the greatest effective quantum number among the excited electrons in the  $t$ th state. In general we can expect to be able to arrange the states of any atom into series in which the quantum defect is roughly constant, and the effective quantum number increases by unity from term to term. This of course can be done with great exactness for atoms with a single excited electron. In general the quantum defect may vary considerably with the  $k$  of the greatest orbit, and with variations in any of the quantum numbers of the other excited orbits, but as a first approximation it will be legitimate to ignore these variations and group together all the terms in  $u(T)$  which have a given principal quantum number for the greatest orbit. We can then write

$$u(T) = \sum_{\tau} (\sum'_t \varpi_t e^{-\{\chi - \chi_t\}/kT}) e^{-\alpha n_{\tau}^6/(r+1)^3}, \quad (19)$$

where  $\Sigma'$  is summed over all states in which the principal quantum numbers of every electron are less than or equal to  $\tau$ , and one at least is equal to  $\tau$ .

To elucidate (19) further we must group together the terms that belong to given numbers of highly excited electrons. Suppose there are  $q$  of these, and  $s$  electrons in all. Then for these states we can ignore  $\chi_t$  and take  $\chi$  to be effectively  $\chi + \dots + \chi_{r+q-1}$ , the energy required to



remove entirely the  $q$  (highly excited) electrons from their normal orbits. Thus these states contribute to  $u(T)$

$$e^{-\{\chi_r + \dots + \chi_{r+q-1}\}/kT} \sum_r (\sum_t' \omega_t) e^{-\pi n_r^2/(r+1)^2}.$$

If we ignore reductions for equivalent orbits which do not affect the term of highest order, we find by (15) and the rules of § 5 that, summed over all states with all  $q$  principal quantum numbers less than or equal to  $\tau$ ,

$$\sum_t' \omega_t = \omega_0^{s-q} \sum_{t_1, t_2, \dots, t_q \leq \tau} t_1^2 t_2^2 \dots t_q^2 \hookrightarrow \frac{\omega_0^{s-q}}{3^q} \tau^{3q}.$$

Therefore, by differentiation,

$$\sum_t' \omega_t \hookrightarrow \frac{3q \omega_0^{s-q}}{3^q} \tau^{3q-1} \dots \dots \dots (20)$$

Hence these states contribute to  $u(T)$

$$\frac{3q \omega_0^{s-q}}{3^q} e^{-\{\chi_r + \dots + \chi_{r+q-1}\}/kT} \sum_r \tau^{3q-1} e^{-\pi n_r^2/(r+1)^2}.$$

In this summation for a first approximation we shall omit the quantum defect and replace the sum by the integral

$$\int_0^\infty \tau^{3q-1} e^{-\pi n^2/(r+1)^2} d\tau,$$

or

$$\frac{1}{6} \Gamma(\frac{1}{2}q) \left\{ \frac{(r+1)^3}{\alpha} \right\}^{\frac{1}{2}q}.$$

The contribution to  $u(T)$  is therefore

$$\Gamma(1 + \frac{1}{2}q) \omega_0^{s-q} \left\{ \frac{(r+1)^3}{9\alpha} \right\}^{\frac{1}{2}q} e^{-\{\chi_r + \dots + \chi_{r+q-1}\}/kT}. \quad (21)$$

There is a similar contribution for every possible value of  $q$ ; the contribution for  $q=0$  (no highly excited orbits) is just  $\omega_0^s$  the weight of the normal and effectively normal states. The complete result may be written, in the usual notation of this paper,

$$u_r^z(T) = \omega_r^z + \sum_{q=1}^{q=s-r} \Gamma(1 + \frac{1}{2}q) \omega_{r+q}^z \left\{ \frac{(r+1)^3}{9\alpha} \right\}^{\frac{1}{2}q} \times e^{-\{\chi_r + \dots + \chi_{r+q-1}\}/kT}. \quad (22)$$

In general it will be found that one term in (22) is dominant for given values of the density and temperature.

In such a case nearly all the atoms  $M_r^z$  present will have just  $q$  highly excited electrons, and the rest in normal orbits, generally forming closed groups. If there is at most a single excited electron ( $q=1$ ), then

$$u_r^z(T) = \varpi_r^z + \frac{\sqrt{\pi\varpi_{r+1}^z}}{2} \left\{ \frac{(r+1)^3}{9\alpha} \right\}^{\frac{1}{2}} e^{-x_r^z/KT}. \quad (23)$$

This is the simplest generalization of the theory of Urey and Fermi. They do not however appear to have noticed the possibility of these simple approximate summations, whose accuracy is ample for most applications.

§ 7. *Variants of the foregoing theory.*—Different methods can be proposed for estimating the excluded volumes. We will expound shortly a variant which has been used for systematic astrophysical work\*, in order to put on record the basis of those calculations. It cannot be claimed to be ultimately correct, so it may be shortly treated, but it seems probable that it does contain a valuable element of the final theory in that it makes the excluded volumes tend to zero as  $T \rightarrow \infty$ . We return to this point later.

Urey and Fermi, in their theory, assume in effect that in the ordinary processes of an assembly in statistical equilibrium the electronic orbits of two distinct atoms cannot in general inter-penstrate. When these orbits are the quickly traversed space-filling orbits of a normal atom we have every reason to believe in this (perhaps non-mechanical) impenetrability, which gives to atoms and matter in general its familiar property of extension. At first sight it is hardly physically convincing to postulate this property for the large nearly degenerate orbits of highly excited atoms. But it may be argued that the only necessary part of this assumption is:—The orbits of the electrons of two distinct atoms, or of an atom and a free electron, never interpenstrate in a collision which fails to change the quantum state of one atom at least. In counting complexions we consistently ignore all processes of exchange, being content with the mere possibility of their occurrence. For the purpose of determining the equilibrium state, the excluded volume of any pair of systems is that region of space into which on the average the other system may not come without causing a change of quantum state. Such an argument may perhaps be held to give some physical reality to the theory of Urey and Fermi. It suggests an alternative method of estimating such excluded volumes.

\* Fowler and Guggenheim, *loc. cit.*

As a possible improvement on the original form, the above analysis suggests that the excluded volumes should be calculated directly from the target areas for transference and ionization by inelastic (and superelastic) collisions according to the ionization theory of Sir J. J. Thomson. These collisions of course in themselves would preserve the perfect gas laws. It is only suggested that the frequency of these collisions indicates the order of the excluded volumes according to their analysis in this section. We need not give details. If  $S_1^2(\zeta)$  represents the target area for a given atom for a successful inelastic impact by a  $\zeta$ -electron, requiring an expenditure  $\zeta_{12}$  of energy, then the average target area for all electronic encounters can be shown to be

$$S_1^{2*} = \frac{e^{-\zeta_{12}/kT}}{(kT)^2} \int_0^\infty e^{-\eta/kT} (\zeta_{12} + \eta) S_1^2(\zeta_{12} + \eta) d\eta. \quad (24)$$

According to Thomson's theory,

$$S_1^2(\zeta) = \frac{\pi \epsilon^4}{\zeta} \left( \frac{1}{\zeta_{12}} - \frac{1}{\zeta} \right),$$

from which we find

$$S_1^{2*} \hookrightarrow \frac{\pi \epsilon^4}{kT \zeta_{12}} \left( \frac{\zeta_{12}}{kT} \text{ small} \right). \quad \dots \quad (25)$$

We now take  $S_1^{2*}$  to be  $\pi R^2$ , where for the moment  $R$  is the radius of the quasi-excluded volume  $v_{a,e}$ , in which a mean has been taken for all electrons. It follows that

$$v_{a,e} \hookrightarrow \frac{4\pi}{3} \frac{\epsilon^6}{(kT \zeta_{12})^{\frac{3}{2}}}. \quad \dots \quad (26)$$

If we calculate  $\overline{R^2}$  or  $\overline{(S_1^2)^{\frac{1}{2}}}$  instead of  $\overline{S_1^2}$ , we get the same result, with an extra factor  $\sqrt{\pi}$ , which is not of serious importance. The energy values of a sequence of optical terms behave like

$$(r+1)^2 R^* hc / (n-\mu)^2,$$

so that when  $n$  is large one may take  $\zeta_{12}$  to be given by

$$\zeta_{12} \hookrightarrow 2(r+1)^2 R^* hc / (n-\mu)^2,$$

and therefore

$$v_{a,e} \hookrightarrow \frac{4\pi}{3} \frac{\epsilon^6 (n-\mu)^{\frac{3}{2}}}{\{2(r+1)^2 R^* hc kT\}^{\frac{3}{2}}}. \quad \dots \quad (27)$$

A similar investigation can be given for the excluded

volume for massive ions, which at sufficiently high temperatures will be dominant owing to their greater charge and smaller speed. We shall not give details here, as, for simplicity, the actual calculations were made without taking these into account.

With a single excited electron, a set of optical states of maximum multiplicity  $2R$  contributes to  $u_r^z(T)$

$$\frac{1}{2^{z-r}} \sum_{K,n} 4RK \exp \left[ -\{\chi_r^z - (\chi_r^z)_{K,n}\} / kT - b_r(n - \mu_K)^{\frac{1}{2}} \right],$$

where

$$b_r = \frac{N}{V} \frac{4\pi}{3} \frac{\epsilon^6}{\{2(r+1)^2 R^* h c k T\}^{\frac{1}{2}}}.$$

The resulting summation after the manner of § 6 leads finally to the expression

$$u_r^z(T) = \varpi_r^z + \frac{1}{2^{z-r}} \left( \sum_R 2R \right) e^{-\chi_r^z / kT} \frac{1}{3} \Gamma(1 + \frac{1}{3}) b_r^{-\frac{1}{3}} \quad (28)$$

The expression  $\sum_R 2R / 2^{z-r}$  is equivalent to  $\varpi_{r+1}^z$  at least in simple cases.

A possible correction for the terms  $(\chi_r^z)_{K,n}$  can be investigated. It leads approximately to an extra factor

$$\exp \left\{ \frac{(r+1)^2 R^* h c}{kT} \left( \frac{4}{9b_r} \right)^{-4/9} \right\}$$

in the second term. This proves to be always so nearly unity that it can be ignored in view of other uncertainties; a similar investigation justifies the neglect of  $\chi_i$  in § 6.

The calculations mentioned were made using (28) on the assumption of just one excited electron, with an estimated value of  $\sum_R (2R)$  for all known optical terms, but with standard weights unity instead of  $1/2^{z-r}$ .

This theory extends very simply to atoms with more than one excited electron. One may presume that each electron has its own excluded volume, in general independent of all the others. This being so, the complete value of  $u(T)$  would be formed by the continued product of expressions like (28), one for each electron, with a maximum multiplicity 2 for each.

§ 8. *Other mean values for excited atoms.*—It is possible to calculate such other mean values derived from  $u(T)$  as may be required by the same process. For example, the average

energy content of any type of atom is given by the standard formula

$$kT^2 \frac{\partial}{\partial T} \log u(T),$$

in which of course only the factors  $(\chi - \chi_i)/kT$  are differentiated. This involves the computation of  $u'(T)$  or, what is the same thing,  $\overline{(\chi - \chi_i)}$ . It is at once obvious that if the normal terms predominate  $\overline{(\chi - \chi_i)} = 0$ , and if the highly excited terms predominate  $\overline{(\chi - \chi_i)} = \chi$ . More precisely (22) yields the equation

$$\frac{du_r^z(T)}{dT} = \sum_{q=1}^{q=\infty-r} (\chi_r^z + \dots + \chi_{r+q-1}^z) \frac{\Gamma(1 + \frac{1}{2}q)}{2^{z-r-q}} \left\{ \frac{(r+1)^{\frac{1}{2}}}{9\alpha} \right\}^{\frac{1}{2}q} \times e^{-\{\chi_r^z + \dots + \chi_{r+q-1}^z\}/kT}; \quad (29)$$

when the term  $q=q^*$  is predominant in (29) and so also in (22) we have

$$kT^2 \frac{\partial}{\partial T} \log u_r^z(T) = \chi_r^z + \dots + \chi_{r+q^*-1}^z. \quad (30)$$

The energy content is the same as if these  $q^*$  electrons were free and at rest relative to the ion. Similar conclusions follow for (23) and (28).

Other expressions which occur in the general formulæ are

$$\frac{1}{V} \sum_{\beta} M_{\beta} v_{\beta, \epsilon}, \quad \frac{1}{Vz} \left[ N \sum_{\beta} M_{\beta} v_{\beta, \epsilon} + \sum_{\alpha, \beta} \frac{M_{\alpha} M_{\beta} v_{\alpha, \beta}}{\sigma_{\alpha, \beta}} \right].$$

These, from their formation by equations (9) and  $p = T \partial \Psi / \partial V$ , can be evaluated as

$$-\sum_{r,z} M_r^z \frac{\partial}{\partial N} \log u_r^z, \quad \frac{1}{2} \sum_{r,z} M_r^z \left( \frac{\partial}{\partial V} - \frac{N}{V} \frac{\partial}{\partial N} \right) \log u_r^z, \quad (31)$$

respectively. In actual applications they are naturally calculated from the summations for the  $u_r^z$ .

The summed form of  $u_r^z$  is given by (22), but it is hardly necessary, for the accuracy suitable to this part of the theory, to retain more than the dominant term  $q=q^*$  in (22). To this approximation,

$$\frac{\partial}{\partial N} \log u_r^z = -\frac{1}{2} q^* \frac{\partial}{\partial N} \log \alpha = -\frac{\frac{1}{2} q^*}{N + \sum_{\beta} M_{\beta}}, \quad (32)$$

$$\left( \frac{\partial}{\partial V} - \frac{N}{V} \frac{\partial}{\partial N} \right) \log u_r^z = \frac{\frac{1}{2} q^*}{V} \frac{2N + \sum_{\beta} M_{\beta}}{N + \sum_{\beta} M_{\beta}}. \quad (33)$$

In general  $q^*$  the average number of bound but highly excited electrons will vary with  $r$  and  $z$  and must be written  $(q_r^z)^*$ . We then find

$$\frac{1}{V} \sum_{\beta} M_{\beta} v_{\beta, \epsilon} = \frac{1}{2} \frac{\sum_{r,z} (q_r^z)^* M_r^z}{N + \sum_{\beta} M_{\beta}}, \quad \dots \dots \dots (34)$$

$$\begin{aligned} \frac{1}{V^2} \left[ N \sum_{\beta} M_{\beta} v_{\beta, \epsilon} + \sum_{\alpha, \beta} \frac{M_{\alpha} M_{\beta} v_{\alpha, \beta}}{\sigma_{\alpha, \beta}} \right] \\ = \frac{\sum_{r,z} (q_r^z)^* M_r^z}{2V} \cdot \frac{N + \frac{1}{2} \sum_{\beta} M_{\beta}}{N + \sum_{\beta} M_{\beta}} \quad \dots (35) \end{aligned}$$

In the variant of the theory described in § 7 there is only one excited electron,  $v_{\alpha, \beta} = 0$  and  $v_{\beta, \epsilon}$  has a different law of variation with quantum number, so that  $\frac{1}{2}(q_r^z)^*$  is replaced by  $\frac{2}{3}$  and all the terms in  $\sum_{\beta} M_{\beta}$  disappear from (34) and (35). The excluded volume corrections are then very easily estimated both for dissociative equilibrium and for pressure. For the former (34) shows that the extra factor  $e^{-J}$  in (11) is such that  $J$  is equal to two-thirds of the ratio of number of massive ions to number of free electrons. This is a number of the order  $1/30$  in stellar interiors and of no importance. For the latter (35) shows an extra term in  $pV/kT$  equal to two-thirds the number of massive ions; this again is only a small correction which is studied in detail in the papers quoted †.

In any form of the generalized theory with any number of highly excited electrons equations (34) and (35) serve to determine these corrections quite simply. They are larger than the corrections for one excited electron, but still not of very great importance in stellar work.

The methods of this section for calculating these corrections can of course be used as soon as  $u_r^*(T)$  has been summed, whatever approximations may have been used in this summation, whether those of § 6, neglecting  $t_0^2$ , or not.

§ 9. *Planck's Theory.*—In an attempt to avoid the arbitrary element in Fermi's theory, Planck ‡ has returned to the Gibbsian phase integral for a mixture of electrons and nuclei, and has approached the problem by direct calculation instead of by attempting to patch up the perfect gas theory. It is still doubtful, in my opinion, whether the

† Fowler and Guggenheim, *loc. cit.*

‡ *Loc. cit.*

correct deductions can be drawn in any simple way, but fundamentally the method of approach must be correct. It will be necessary to discuss and generalize Planck's calculations here. We will start by briefly restating his theory for massive point charges  $+Ze$  and free and bound electrons, assuming for simplicity at this stage that at most one electron per nucleus is bound.

The classical phase integral for a single movable electron and fixed nucleus is

$$F = \frac{1}{h^3} \iiint e^{-\eta/kT} p^2 dp d\Omega_p r^2 dr d\Omega_r, \quad (36)$$

where

$$\eta = \frac{1}{2m} p^2 - \frac{Ze^2}{r}. \quad (37)$$

$\Omega_p$  and  $\Omega_r$  are elements of solid angle defining the directions of the momentum and position vectors. Thus  $F$  can be written:

$$F = \frac{\sqrt{(2m^3)}}{h^3} \iiint e^{-\eta/kT} (\eta r^2 + Ze^2 r)^{\frac{1}{2}} r dr d\eta d\Omega_r d\Omega_p.$$

Let  $V$ , the volume available to the electron, be a sphere of radius  $A$ , and suppose that an  $\eta'$  can be chosen so that

$$Ze^2/A \leq \eta' \leq kT. \quad (I.)$$

Then the contributions to  $F$  can be divided into three parts:—

- |             |                             |              |                        |
|-------------|-----------------------------|--------------|------------------------|
| (1) $F_1$ . | $\infty > \eta > 0$ .       | Dissociated. | Classical.             |
| (2) $F_2$ . | $0 > \eta > -\eta'$ .       | Combined.    | Effectively Classical. |
| (3) $F_3$ . | $-\eta' > \eta > -\infty$ . | Combined.    | Quantized.             |

In (3) the phase integral must be replaced by a summation over the possible stationary states.

(1) In  $F_1$  we have  $\eta \gg Ze^2/r$  over practically the whole of the effective domain of integration. Hence we replace the factor  $(\eta r^2 + Ze^2 r)^{\frac{1}{2}}$  by  $\eta^{\frac{1}{2}} r$ , and find

$$F_1 = \frac{(2\pi m kT)^{\frac{3}{2}} V}{h^3}, \quad (38)$$

which is the ordinary partition function for the free electron.

(2) In  $F_2$  we have effectively  $\eta/kT = 0$ . Putting  $\alpha = -\eta$ , we find

$$F_2 = \frac{16\pi^2 \sqrt{(2m^3)}}{h^3} \int_0^{\eta'} d\alpha \int_0^a (Ze^2 r - \alpha r^2)^{\frac{1}{2}} r dr, \quad (39)$$

where  $a$  is the smaller of  $Ze^2/\alpha$  and  $A$ .

(3) In  $F_3$  we have to replace the phase integral by the quantum sum :

$$F_3 = \sum_1^{n'} n(n+1) e^{-\chi_n/kT} \quad (\chi_n = R^*hcZ^2/n^2), \quad . \quad . \quad (40)$$

where  $n' = (R^*hcZ^2/\eta')^{\frac{1}{2}}$ .

Thus far Planck. He points out further that under assumption (1.)  $F_2 \leq F_1$ , and argues that  $F_2$  can therefore be neglected. It does not appear to me that this is logical. It seems rather that the condition for neglecting  $F_2$  is  $F_2 \ll F_3$ , and this is *not* guaranteed by (1.). It appears to me necessary (or at the least preferable) to calculate  $F_2$  exactly (this is easy) and to use  $F_2 + F_3$  as the contribution from the bound orbits of the electron. In  $F_2$  put  $r = (Ze^2/\alpha) \sin^2 \phi$ . Then

$$F_2 = \frac{32\pi^2 \sqrt{(2m^3)}}{h^3} (Ze^2)^3 \int_0^{\eta'} \frac{d\alpha}{\alpha^{\frac{5}{2}}} \int_0^a \sin^4 \phi \cos^2 \phi d\phi,$$

where  $a$  is  $\arcsin(\alpha A / Ze^2)^{\frac{1}{2}}$ , if this is real, or else  $\frac{1}{2}\pi$ . The double integral therefore divides into

$$\int_0^{Ze^2/A} \frac{d\alpha}{\alpha^{\frac{5}{2}}} \int_0^{\arcsin(\alpha A / Ze^2)^{\frac{1}{2}}} \sin^4 \phi \cos^2 \phi d\phi + \int_{Ze^2/A}^{\eta'} \frac{\pi}{32} \frac{d\alpha}{\alpha^{\frac{5}{2}}}$$

or

$$\frac{2}{(Ze^2/A)^{\frac{3}{2}}} \int_0^{\frac{1}{2}\pi} \frac{\cos \theta d\theta}{\sin^4 \theta} \int_0^{\theta} \sin^4 \phi \cos^2 \phi d\phi + \frac{\pi}{32} \int_{Ze^2/A}^{\eta'} \frac{d\alpha}{\alpha^{\frac{5}{2}}}.$$

The last double integral can be evaluated by integration by parts. It is

$$-\frac{1}{3} \int_0^{\frac{1}{2}\pi} \sin^4 \phi \cos^2 \phi d\phi + \frac{1}{3} \int_0^{\frac{1}{2}\pi} \frac{d\theta}{\sin^3 \theta} \sin^4 \theta \cos^2 \theta = \frac{1}{9} - \frac{\pi}{96}.$$

Thus

$$\begin{aligned} F_2 &= \frac{32\pi^2 \sqrt{(2m^3)} (Ze^2)^3}{h^3} \left[ \frac{2}{9} \frac{A^{\frac{3}{2}}}{(Ze^2)^{\frac{3}{2}}} - \frac{\pi}{48} \frac{1}{(\eta')^{\frac{3}{2}}} \right], \\ &= Z^3 (R^*hc)^{\frac{3}{2}} \left[ \frac{32}{9\pi} \frac{A^{\frac{3}{2}}}{(Ze^2)^{\frac{3}{2}}} - \frac{1}{3} \frac{1}{(\eta')^{\frac{3}{2}}} \right]. \quad . \quad . \quad . \quad (41) \end{aligned}$$

Now by the arguments of former sections we have approximately

$$F_2 = 2e^{\chi_1/kT} + \frac{1}{3} n'^3. \quad . \quad . \quad . \quad (42)$$



Therefore combining (41) and (42) we have

$$e^{x_1/kT} u(T) = F_2 + F_3 = 2e^{x_1/kT} + \frac{32}{9\pi} \frac{(ZR^*hcA)^{\frac{1}{2}}}{\epsilon^3}. \quad (43)$$

This is the partition function for the one bound electron. The second term will generally be dominant for large  $T$ , in which case Planck's discussion seems inadequate.

When the assembly contains a number of fixed nuclei and one electron,  $F$  is still given by (36) with

$$\eta = \frac{1}{2m} p^2 - \sum_a \frac{Z\epsilon^2}{r_a}. \quad (44)$$

The electron can only be *bound* to one nucleus at a time, and the suggestion made by Planck is equivalent to asserting that *when  $\eta < 0$  the electron is bound to the nearest nucleus*. Each nucleus then makes a contribution like (43) to  $F$ , which may be described by saying that each nucleus has this partition function for a bound electron, if  $A$  is so chosen that on the average the bound electron is nearer to the selected nucleus than to any other. If there are  $M$  nuclei we must therefore take

$$M \cdot \frac{4}{3}\pi A^3 = V. \quad (45)$$

The essential part of (I.) is then the condition

$$Z\epsilon^2 \left( \frac{M}{V} \right)^{\frac{1}{3}} \ll kT. \quad (II.)$$

Planck's suggestion can now be generalized for a number of nuclei of different positive charges. The condition that the electron should be bound to nucleus 1 rather than to nucleus 2 is now naturally

$$Z_1/r_1 > Z_2/r_2.$$

This means that to each nucleus ( $Z$ ) we must now attach a mean volume proportional to  $Z^3$ . If we now define a radius  $A$  by the equation

$$\frac{4}{3}\pi A^3 \sum_z Z^3 M^z = V \quad (46)$$

then the actual radius  $A_1$  for use in (43) for a nucleus  $Z_1$  will be

$$A_1^3 = \frac{3}{4\pi} \frac{Z_1^3 V}{\sum_z Z^3 M^z}. \quad (47)$$

The partition function for the nucleus  $Z_1$  in general may

therefore be written

$$F_2 + F_3 = 2e^{x_1/kT} + \left[ \frac{32}{9\pi} \left( \frac{3}{4\pi} \right)^{\frac{1}{2}} \frac{(R^*hc)^{\frac{3}{2}}}{\epsilon^3} \right] \frac{Z_1^3 V^{\frac{1}{2}}}{(\sum_z Z^3 M^z)^{\frac{1}{2}}} \quad (48)$$

The value of the permanent constant in [ ], to be written B, is  $5.086 \times 10^{11}$ .

On the rest of Planck's development allowing of more than one electron and moving nuclei it is not necessary to comment here, so long as we do not allow any one nucleus to capture more than one electron, and are prepared to ignore the effect of this movement on the rule for fixing the particular nucleus to which an electron is bound. In our notation therefore

$$u_{z_1-1}^z(T) = 2 + B \frac{Z_1^3 V^{\frac{1}{2}}}{(\sum_z Z^3 M^z)^{\frac{1}{2}}} e^{-x_{z_1-1}^z/kT}. \quad (49)$$

To extend the argument to the capture of more than one electron is not difficult, provided rather rough approximations are allowed. We shall obviously approximate fairly closely to the catching power of an atomic ion for its  $t$ th electron by assuming that it captures like a point charge  $(Z-t+1)e$ . This will of course be close to the truth when the previously caught electrons are in orbits of less excitation than the  $t$ th. In general it must *underestimate* the efficiency of the ion for capture of the next electron. An *overestimate* of the efficiency can be made by assuming that the ion captures like a point charge  $(Z-t')e$ , where  $t'$  is the number of electrons practically always in normal orbits (usually closed groups). In many applications these two limits will not be widely different, but the former may be expected to be the better approximation. With the weights laid down in § 5 the two parts  $F_2$  and  $F_3$  fit together as before for each stage of capture.

In order to estimate the value of  $u_r^z(T)$  we proceed as in § 6 and consider separately the parts arising for various specified numbers  $q$  of highly excited electrons. When there are no highly excited electrons the weight of the normal state is no longer 2 but  $\varpi_r^z$ . When there are  $q$  highly excited electrons the weight of the remaining core is no longer unity but  $\varpi_{r+q}^z$ . Under the assumptions we have made, ignoring reductions for equivalent orbits, the contribution for  $q$  such electrons will be equal to the continued product of the contributions for each of the  $q$  electrons in order, with an extra factor  $\varpi_{r+q}^z$  for the weight of the core. According therefore

to the assumed catching power of the ion we find the following forms for  $u_r^z(T)$  :—

$$u_r^z(T) = \varpi_r^z + \sum_{q=1}^{q=z-r} \varpi_{r+q}^z (r+1)^{3q} B^q \left\{ \frac{V}{\sum_{r,z,q} (r+1)^3 M_r^z} \right\}^{1/2} \\ \times e^{-\{x_r^z + \dots + x_{r+q-1}^z\}/kT}, \quad (50 a)$$

$$u_r^z(T) = \varpi_r^z + \sum_{q=1}^{z-r} \varpi_{r+q}^z (r+1)^{3q} B^q \left\{ \frac{V}{\sum_{r,z,q} (r+q)^3 (M_r^z)_q} \right\}^{1/2} \\ \times e^{-\{x_r^z + \dots + x_{r+q-1}^z\}/kT}. \quad (50 b)$$

In (50 b)  $(M_r^z)_q$  is the average number of atomic ions of atomic number  $Z$ ,  $r$  times ionized, with  $q$  highly excited electrons. Equations (50 a) and (50 b) are derived respectively from lower and upper limits of the catching power. A closer approximation than either to the catching power can probably be obtained as follows. Consider the normal ion with  $z-r-q$  electrons in normal orbits and let it catch  $q$  more electrons in succession into highly excited orbits, assuming at each step that the number of possible orbits so obtained is not altered by later captures. Such a calculation will have the effect of replacing  $(r+1)^q$  in (50 a) by  $(r+1) \dots (r+q)$ , and we obtain the approximation :

$$u_r^z(T) = \varpi_r^z + \sum_{q=1}^{q=z-r} \varpi_{r+q}^z (r+1)^3 \dots (r+q)^3 B^q \\ \times \left\{ \frac{V}{\sum_{r,z,q} (r+1)^3 \dots (r+q)^3 (M_r^z)_q} \right\}^{1/2} e^{-\{x_r^z + \dots + x_{r+q-1}^z\}/kT}. \\ \dots \dots \dots (50 c)$$

In this approximation, which may be preferred to (50 a) or (50 b) in applications, we assert that an  $(M_r^z)_q$  has caught electrons and possesses such a number of possible orbits within its radius of action as if it were a point charge  $(r+1)^{\frac{1}{q}} \dots (r+q)^{\frac{1}{q}} e$ .

These  $u_r^z(T)$  of Planck's theory may be used for a direct construction of the characteristic function  $\Psi$  of the assembly.

If  $F_r^z$  and  $G$  are given by equations (5) with the values of this section for  $u_r^z(T)$ , then

$$\Psi/k = N \left( \log \frac{VG}{N} + 1 \right) + \sum_{r,z} M_r^z \left( \log \frac{VF_r^z}{M_r^z} + 1 \right), \quad (51)$$

to which radiation and electrostatic terms may be added as in equation (8). There are in this theory as here developed no excluded volumes.

In applications the most important combination is  $u_{r+1}^z(T)/u_r^z(T)$ . It will be found that in general one term of (50) is dominant for given density and temperature, and that the dominant terms of  $u_{r+1}^z(T)$  and  $u_r^z(T)$  generally correspond to equal numbers of electrons in normal orbits, and the loss of one excited electron by the  $M_{r+1}^z$ . In this case

$$\frac{u_{r+1}^z(T)}{u_r^z(T)} = \frac{e^{x_r^z/kT}}{(r+1)^3 B} \left\{ \frac{V}{\sum_{r,z,q} (r+1)^3 \dots (r+q)^3 (M_r^z)^q} \right\}^{-1}. \quad (52)$$

If  $s$  is the average number of free electrons per atom, then

$$\sum_{r,z} r M_r^z = s \sum_{r,z} M_r^z = N.$$

It will then be permissible as a first very rough approximation to write

$$\sum_{r,z,q} (r+1)^3 \dots (r+q)^3 (M_r^z)^q = (s+1)^3 \sum_{r,z} M_r^z = (s+1)^2 N,$$

and so

$$\frac{u_{r+1}^z(T)}{u_r^z(T)} = \frac{(s+1) e^{x_r^z/kT}}{(r+1)^3 B (V/N)^{\frac{1}{3}}}. \quad (53)$$

Other combinations can be derived from the  $u_r^z(T)$  as in § 8.

§ 10. *Comparisons of the foregoing theories.*—A comparison of the foregoing theories can be simply made for the case of a single excited electron. We then have the following results, in which the permanent constants have been given numerical values.

Theory of Urey and Fermi :

$$u_r^z(T) = \varpi_r^z + 3.70 \times 10^{11} \varpi_{r+1}^z (r+1)^{\frac{3}{2}} (V/N)^{\frac{1}{2}} e^{-\chi_r^z/kT}. \quad (54 a)$$

Theory of Planck :

$$u_r^z(T) = \varpi_r^z + 5.09 \times 10^{11} \varpi_{r+1}^z \frac{(r+1)^3}{s+1} \left(\frac{V}{N}\right)^{\frac{1}{2}} e^{-\chi_r^z/kT}. \quad (54 b)$$

Variant of § 7 :

$$u_r^z(T) = \varpi_r^z + 1.45 \times 10^{10} \varpi_{r+1}^z (r+1)^3 T \left(\frac{V}{N}\right)^{\frac{1}{2}} e^{-\chi_r^z/kT}. \quad (54 c)$$

In stellar applications  $T$  varies from  $10^6$  to  $5.10^7$  and  $(N/V)^{\frac{1}{2}}$  from perhaps  $10^8$  to  $10^4$ . There is therefore an extra numerical factor of average value 2000 or so to be inserted in the last formula for a direct comparison in such cases. The numerical factor in the last formula is therefore greater by a factor of rather more than 50 than those of the first two, which may be said to agree. Since, however, the only important function of the  $u$ 's in applications is  $u_{r+1}^z/u_r^z$  the absolute value of the coefficients will only matter in determining the temperature at which the relative importance of the two terms in  $u_r^z$  reverses. It is easy to see that the use of any one of these formulæ would lead to almost indistinguishable astrophysical results \*. Choice of theory is of minor importance if there is to be only one excited electron.

It appears, however, that the absolute value of the constant at once becomes of major importance when there may be any number of excited electrons and choice of the truest theory imperative. It is impossible to believe that there must be only one excited electron. The more general calculation of the  $u$ 's here contemplated will have to be used, and it must be presumed that Planck's theory, as given here, is probably the best yet formulated.

The difference of form, however, between (54 b) and (54 c) suggest that some further modification of Planck's theory may be desirable before extensive astrophysical calculations are undertaken. The  $T$ -factor in (54 c) arises from the relative velocity of the interacting systems—the greater

\* Cf. the calculations of Guggenheim, *loc. cit.*

the relative velocity the less the target area, after a certain minimum is exceeded. Such an effect must really be present. The absence of such a factor from Planck's formula is due to this calculation being based on point nuclei *at rest*, unmodified when they are allowed to move. If, however, the nuclei are in relative motion, then it will not necessarily be the nearest which limits the catching region of the nucleus under consideration. Relative to this nearest the energy of the electron need not even be negative. At temperatures sufficiently high the relative motion of the nuclei must become important in increasing the sizes of catching regions. The effect awaits exact investigation. If this is possible in any simple manner, Planck's theory so modified would appear to provide a satisfactory approximation to the true partition functions for atomic ions.

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LXXVI. *On the Choice of Striking Point in the Pianoforte String.* By R. N. GHOSH, M.Sc., Lecturer in Physics, Allahabad University\*.

[Plate XIII.]

**I**N a series of papers† it has been shown that the elasticity of the hammer-felt must be taken into consideration to calculate the duration of impact. It is this quantity which controls the quality of the note. The amplitude of partials, their duration, etc., depend upon this. The variation of the tone quality also depends upon the power of changing the duration of impact by "touch." In this paper a preliminary account is given of the experimental investigation on the amplitudes of the partials from a steel string struck at different points, and a comparison has also been made with the theory as given in Phil. Mag. vol. xlix. p. 121 (1925), the result of which is to indicate that the choice of the striking point should be such as to make the ratio of the free period of vibration of the string to the duration of impact equal to 2. Very recently some work has been done in this

\* Communicated by Prof. Megh Nad Saha.

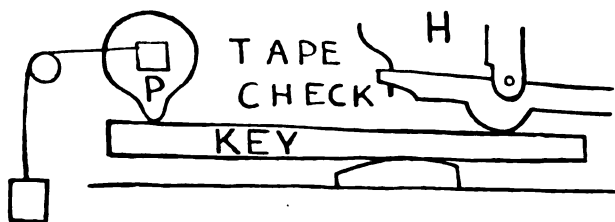
† Phil. Mag. vol. xlvii. p. 1142 (1924); vol. xlix. p. 121 (1925).  
Proc. Ind. Assoc. Calcutta, vol. x. pt. 1.

direction by others\*, but little attention has been paid to the correlation of the results with the theory.

*Experimental Methods.*

A piano string was fixed over two bridges on a sonometer and kept vertical by suitable supports. The string was struck by a pianoforte hammer and key which were taken out from an actual pianoforte. The system used was a tape check action. The variation of the striking point was made by raising or lowering the sonometer. It was always carefully arranged that the hammer had full play, for if the hammer was very close to the string the note was dull. The point struck was photographed by a falling plate; in some cases the trace of an electrically maintained tuning-fork was simultaneously photographed to obtain the duration of contact. In order to strike the key always with the same force, or to give the hammer the same velocity, a very simple arrangement was made, shown diagrammatically in fig. 1.

Fig. 1.



To a wooden axle a wheel  $p$  of the shape shown was fixed just over the key; it was arranged that a kilogram load should always fall through a height of 10 cm. and give one revolution to the wheel, which presses the key instantaneously, thus giving the hammer always the same velocity. The frequency of vibration of the string was found out from the plates in which the simultaneous record of the tuning-fork was obtained. Having no mechanical analyser, the curves were analysed by the schedule method given by H. O. Taylor (Phys. Review, Oct. 1915). For this purpose the curves were magnified 50 times and a faithful trace was taken, then the ordinates were carefully measured. Below is given a table of the amplitudes of five components with different hammers at different points. For the sake of comparison the duration of contact is also given there.

\* Phil. Mag. vol. 1. p. 491 (1925). Proc. Ind. Assoc. vol. viii. pt. 2.

TABLE I.

Length of the string 100 cm. Freq. 88 per second.  
Mass per unit length .0961 gm. per cm.  
Velocity of impact  $2 \times 10$  cm. per sec.

No.	$a$ .	$\frac{T}{\phi}$	Hammer No.	1.	2.	3.	4.	5.	Remarks.
1 .....	8	2.3	1	1.33	1.09	.078	.122	.21	
2 .....	11	1.85	1	3.16	2.75	.96	1.06	.031	Fund. max.
3 .....	12.5	1.80	1	2.9	2.6	.90	.91	.24	
4 .....	14	1.56	1	1.8	1.3	.78	.71	.25	
5 .....	16.5	1.44	1	3.07	1.7	.62	.31	.20	
6 .....	20.5	1.1	1	3.66	1.34	.50	.27	.09	Fund. max.
7 .....	12	1.08	3	2.08	1.05	.78	.297	.08	
8 .....	15.2	.97	3	3.4	1.2	.71	.144	.37	
9 .....	17	.91	3	5.09	1.82	.84	.13	0	
10 .....	20	.83	3	5.74	1.08	1.36	.31	0	
11 .....	11.3	2.9	5	.404	1.12	1.15	.25	.13	
12 .....	15.7	2.4	5	1.98	1.48	.47	.29	.30	
13 .....	19	2.1	5	3.29	2.06	.72	.17	.086	Fund. max.

$a$  = Striking distance from nearer bridge.

$\frac{T}{\phi}$  = Free period of vibration of string / duration of impact.

Effective mass of hammer No. 1 = 7.1 gm.  $\frac{T}{\mu} = 1.3$ .  
 „ „ „ No. 3 = 19.0 gm.  $\frac{T}{\mu} = .56$ .  
 „ „ „ No. 5 = 2.6 gm.  $\frac{T}{\mu} = 0$ .

### Discussion of Results.

The simple formula for the amplitude of any component has been given in Phys. Review, vol. xxiv. p. 456 (1924). For the same string and the same velocity of impact, the amplitude of the  $s$ th component at the point struck is given by

$$A_s = - \frac{\sin^3 s\pi a/l \cdot \cos (s\pi\phi/T)^*}{s(s^2 - \frac{1}{4}T^2/\phi^2)}, \quad \dots (1)$$

discarding quantities which are small.

\* Recently the author has been able to make further approximations in the formula.



TABLE II.— $l=100$ . Freq. 124.  $\rho = .0211$ . Velocities of impact arbitrary.

No.	$\alpha$	$\frac{T}{\phi}$	1.	2.	3.	4.	5.	6.	7.	8.	9.	Hammer No.
1	.....	.....	1	.24	.111	.072	.047	.03	.033	.37	.36	5
2	.....	.....	1	.23	.12	.022	.048	.02	.015	.13	.02	5
3	.....	.....	1	.51	.29	.091	.094	.07	.016	.018	.03	5
4	.....	.....	1	.34	.098	.095	.041	.106	.032	.034	.01	5
5	.....	.....	1	.18	.24	.048	.014	.037	.038	.007	.02	1
6	.....	.....	1	.01	.18	.068	.042	.043	.01	.008	.003	1
7	.....	.....	1	.09	.012	.04	.007	.023	.02	.018	.18	1
8	.....	.....	1	.15	.092	.11	.059	.042	.19	.015	.009	1

TABLE III.— $l=100$ . Freq. 84.  $\rho = .0795$ .

No.	$\alpha$	$\frac{T}{\phi}$	1.	2.	3.	4.	5.	6.	7.	8.	9.	Hammer No.
1	.....	1.55	1	.41	.185	.103	.08	.018	.01	.032	.049	1
2	.....	1.67	1	.31	.164	.10	.05	.20	.013	.023	.06	1
3	.....	1.86	1	.69	.083	.17	.12	.04	.017	.017	.041	1
4	.....	1.97	1	1.03	.285	.19	.05	.162	.054	.033	.13	1
5	.....	2.48	1	.98	.32	.103	.114	.074	.062	.069	.042	5
6	.....	2.74	1	.75	.66	.25	.25	.031	.08	.023	.07	5
7	.....	2.95	1	1.8	1.2	.63	.05	.11	.146	.035	.06	5
8	.....	3.1	1	1.84	1.03	.53	.54	.28	.095	.054	.09	5

$$\frac{T}{\mu} = .11 \text{ for } H_1.$$

Below is given a table of the amplitudes of the fundamental and the octave for different values of  $\frac{T}{\phi}$  for the same value of  $\alpha$  calculated from (1).

TABLE IV.

No.	$\frac{T}{\phi}$	1.	2.	3.	Remarks.
1 .....	·5	1·06	·125	.....	Fundamental max.
2 .....	·7	·3	·12	.....	
3 .....	1·0	1·33	·133	·04	Fundamental max.
4 .....	1·5	·43	·08	.....	
5 .....	1·7	1·0	·13	.....	
6 .....	2	1	·17	.....	Fundamental max.
7 .....	2·5	·55	·20	.....	
8 .....	3	·4	·14	·049	

From Table I. we find that the fundamental is maximum at  $\frac{T}{\phi} = 1$ , and  $\frac{T}{\phi} = 2$ , which are theoretically required when

$$\sin^2 \frac{s\pi\alpha}{l}$$

remains the same. In the experiments that have been tabulated the ratio  $\frac{T}{\phi}$  was changed, firstly by changing the striking distance and secondly by changing the hammer.

$$\frac{T}{\phi} = \frac{1}{\pi N} \left( \frac{T}{M} \right)^{\frac{1}{2}} \left\{ \frac{1}{\alpha(1 + T/\mu\alpha)} - \frac{1}{4} \frac{\rho}{M} \right\}^{\frac{1}{2}} \cdot \cdot \cdot \quad (2)$$

$$M = M_0 + \frac{\rho\alpha}{3} = \text{effective mass of hammer.}$$

$N$  = frequency,  $T$  = tension.

A correct comparison of Table IV. with Tables I., II., and III. can only be made when the amplitudes tabulated there are divided by  $\sin^2 \frac{s\pi\alpha}{l}$ ,

$$A_s = \frac{A_s \text{ obs.}}{\sin^2 \frac{s\pi\alpha}{l}} \cdot \cdot \cdot \cdot \cdot \cdot \quad (3)$$

The presence of the factor  $\sin^2 \frac{s\pi\alpha}{l}$  is to increase the

amplitude as we move away from the bridge. If the variation of the amplitude due to change of  $\frac{T}{\phi}$  with change of  $\alpha$  is much larger than the increase of  $\sin^2 \frac{s\pi\alpha}{l}$ , the rise and fall of amplitude will still be found. And this is the case in hammers No. 1 and 5, while in the case of hammer No. 3 the amplitudes go on increasing with increase of  $\alpha$ . This, as just now pointed out, is due to the fact that the percentage variation of the amplitude due to change in  $\frac{T}{\phi}$  is smaller than that of the increase due to  $\sin^2 \frac{s\pi\alpha}{l}$ . In other words, the effect is masked. At 20 cm. from the bridge in the case of H. 5,  $\frac{T}{\phi} = 2.1$ , while in the case of H. 1,  $\frac{T}{\phi} = 1.1$ ; so that  $\sin^2 \frac{s\pi\alpha}{l}$  remains the same in both the cases and the amplitudes of the fundamental, the octave, and the second harmonic are related as

TABLE V.

3 : 1 : 5/30 for H. 1.

3 : 2 : 7/30 for H. 5.

Hence we find that, though the maximum of the fundamental is almost the same in the case when  $\frac{T}{\phi} = 1$ , or when  $\frac{T}{\phi} = 2$ , the octave and the third components increase in amplitude when  $\frac{T}{\phi} = 2$ . Lastly, reducing the amplitudes to the same scale we obtain

TABLE VI.

	H. 1.	H. 3.	} $\frac{T}{\phi} = 1.$
1 .....	11	14	
2 .....	4	7.5	
3 .....	1.4	5.0	

According to the simple theory calculated in Table IV. the amplitudes should be equal, but there are other factors, namely, the stiffness of the string, the reflexions which

influence the amplitudes to a large extent and which we have not taken into consideration. From Table IV. we also find that the amplitude of the fundamental is again maximum when  $\frac{T}{\phi} = \frac{1}{2}$ . This was not experimentally verified, but the ratio  $\frac{T}{\phi} = \frac{1}{2}$  does not seem to be of practical use, for then the reflexions from the farther end in presence of the hammer on the string would render the partials non-harmonic. Discarding this case, we must have the ratio  $\frac{T}{\phi} = 1$  or 2 to have a large fundamental.

*Choice of the Striking Point.*—From Table V. we find that the amplitude of the octave and the third component in the case  $\frac{T}{\phi} = 2$  is greater than in the case  $\frac{T}{\phi} = 1$ . The presence of the third component is theoretically explained by the second term in equation 16 (Phil. Mag. vol. xlix. p. 128, 1925). Further, in this case the impact ceases before the wave reaches the other end. From these considerations it seems, therefore, that the choice of the striking point is made by making the ratio  $\frac{T}{\phi} = 2$ . This had been verified in the case of the piano which I possess. The ratio  $\frac{T}{\phi}$  was calculated from formula (2).

$l = 91.5$  cm.  $\rho = .137$  grm. per cm.

Tension  $= 4.57 \times 10^7$ .

Freq. 100 approx.

Maxima at 11.1 cm. (experimentally found).

Mass of hammer 10.5 gm.

$\frac{T}{\phi} = 1.87$ . [From (2).]

Hence we see that the choice of the striking point depends upon the ratio  $\frac{T}{\phi}$  which must be 2 : 1.

This ratio can be achieved in practice in two ways, viz., by changing the mass of the hammer or the striking distance so that their product remains constant. Now  $\alpha$  the striking distance should not be greater than a finite value, otherwise the waves undergo modifications from reflexions from the farther end and the components would be rendered

non-harmonic for reasons mentioned before. Also  $\alpha$  should not be very small, for on account of the factor  $\sin \frac{\pi \alpha}{l}$  the amplitude of the resulting vibrations would be very small. Hence  $\alpha$  must lie somewhere between  $1/9$  to  $1/7 l$ . When  $\alpha$  is fixed the mass of the hammer is determinate. For the best musical note the partials must converge in a particular way. For a given value of  $\frac{T}{\phi}$  the convergence of the partials is the same when  $\sin \frac{\pi \alpha}{l}$  is constant. But on account of the latter factor the convergence is different at different points, even if  $\frac{T}{\phi}$  is made the same at different points of the string by arranging so that the product of the mass of the hammer and the striking distance remains the same. The value of  $\alpha$  for the best musical effect, therefore, also depends upon the factor  $\sin \frac{\pi \alpha}{l}$ . This point is under investigation with the help of a piano tuner.

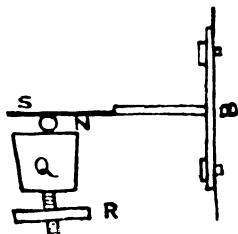
Coming back to the comparison of Tables III. and IV., we find that the ratio of the amplitudes of the fundamental and the octave is the same for a given value of  $\frac{T}{\phi}$  as indicated in Table IV., *e.g.* when  $\frac{T}{\phi} = 1.55$  the theoretical value of the ratio is .44, and experimentally it is found to be .41. Again, when  $\frac{T}{\phi} = 2$ , the ratio is 1.17 and experimentally it is 1.03; when  $\frac{T}{\phi} = 1.7$ , the ratios are .6 and .3. Similarly the theoretical conclusions for other values of  $\frac{T}{\phi}$  are approximately verified experimentally.

#### *Sound Board.*

The effect of varying the striking point on the string on the amplitude of vibration on the sound-board was also investigated. For this purpose a piano whose front part was taken away was used. The velocity of impact was kept constant by the key and wheel arrangement described before. For photographing the vibrations of the sound-board, a steel strip S was soldered to a thick piece B perpendicularly and the piece was screwed to the sound-board. The strip pressed against a rolling needle N supported on a screw top which could be raised or lowered at pleasure:

this was firmly kept in position by another nut R. To the rolling needle a small concave mirror was attached, and a spot of light from an arc lamp was focussed on the moving photographic plate. Pl. XIII. figs. 3, 4, 5, 6, &c. show the vibration curves at different striking points for the same velocity of impact. One very striking phenomenon is the rise and fall of the amplitude of vibration. In some cases the amplitudes

Fig. 2.



swell out first and then diminish steadily. At other points the amplitude passes through small rise and fall and then attains the maximum value, after which there is a steady fall. When the striking distance is small the rise and fall do not appear to be marked, but at greater distances the number of rise and fall and the variation are very marked, as can be observed from the pictures (the photographic plate was dragged at approximately the same velocity). A fuller account with the theory of the vibrations of sound-board will be presented shortly.

Measurements were taken of the biggest amplitude at different points and the average values are tabulated below:—

No.	$\frac{\alpha}{l}$	Amplitude.	Reduced amplitude.
1 .....	$\frac{1}{10}$	1.4	4.5
2 .....	$\frac{1}{8.3}$	1.75	4.9
3 .....	$\frac{1}{7.3}$	1.4	3.4
4 .....	$\frac{1}{6.3}$	1.9	3.8
5 .....	$\frac{1}{5.5}$	1.4	2.6
6 .....	$\frac{1}{5.3}$	2.0	3.6
7 .....	$\frac{1}{4.6}$	2.4	3.8
8 .....	$\frac{1}{4}$	2.8	3.8

The amplitudes at different points undergo a variation on account of the change in the value of  $\sin \frac{\pi \alpha}{l}$ , and hence they must be reduced to the same scale by dividing them with  $\sin \frac{\pi \alpha}{l}$ ; column 3 was obtained in this way, and we find that the amplitude is maximum at  $\frac{\alpha}{l} = \frac{1}{8.3}$ .

The vibration that results in the sound-board is a forced vibration, and it is expected that the maximum forced vibration would result when the force is maximum. Now we have seen that at  $\alpha = 11.1$  the ratio  $\frac{T}{\phi}$  for the same piano string and hammer system is 2. Hence the effect observed is simply due to the maximum force on the bridge due to the maximum vibration of the string. The sound-board shown by Berry\* has a minimum free vibration at this place.

#### *Conclusion.*

The experimental results of analysis of different vibration curves obtained by striking the string at different points with the same velocity are:—

- (1) Fundamental is maximum when  $\frac{T}{\phi} = 1$ .
- (2) Fundamental is maximum when  $\frac{T}{\phi} = 2$ .
- (3) The first and second harmonics are stronger in case 2 than in 1.
- (4) Choice of the striking point in the piano is made in such a way so as to obtain  $\frac{T}{\phi} = 2$ .
- (5) The sound-board reproduces the maximum vibration of the string at  $\frac{T}{\phi} = 2$ .
- (6) The choice of the striking point should be such that it lies between  $1/9$  to  $1/7$  of the length of the string.

\* Phil. Mag. xix. p. 647 (1910).

*Refractive Index of Gases and Vapours in Magnetic Field.* 885

The author begs to record his debt of gratitude to Prof. M. N. Saha for his kindly supplying him with a pianoforte.

Physics Department,  
Allahabad University.  
September 17, 1925.

*Note added in proof.*

Further extensions of Table (I.) :—

$l=95$  cm. Freq. 130,  $\rho=0.22$  gm. per cm.

$T=1.34 \times 10^7$ .  $\alpha=11$  cm. Const.

No.	$\frac{T}{\phi}$	1.	2.	3.	Remarks.
1 { .....	1.3	4.7	1.2	1.1	
2 .....	.98	4.8	1.1	.32	
3 .....	.52	1.27	1.48	.69	Different hammers.
4 .....	.82	4.3	.69	.56	
5 .....	1.1	4.9	1.0	.40	

$l=92$  cm.  $T=1.88 \times 10^7$ . Freq.=160.

$T=0$ .  $M=2.6$  gm. Const.  
 $\mu$

No.	$\alpha$ .	$T$ $\phi$	Reduced amplitude.		
			1	2	3
1 .....	6	1.9	23.5	6.2	.42
2 .....	8	1.62	23.3	4.0	.93
3 .....	11	1.36	18.1	1.4	.46
4 .....	16	1.1	20.2	.6	.38
5 .....	18.5	.95	15.0	1.1	1.07

LXXVII. *The Refractive Index of Gases and Vapours in a Magnetic Field.* By RONALD FRASER, B.Sc., Assistant in Natural Philosophy at the University of Aberdeen\*.

*Introduction.*

THE experiments of Gerlach and Stern † have shown that certain atoms are orientated in a magnetic field in accordance with the theory of space quantization developed by Sommerfeld. On the other hand, Glaser's results on

\* Communicated by Prof. G. P. Thomson, M.A.

† Gerlach and Stern, *Ann. Phys.* lxxiv. p. 673 (1924); Gerlach, *ibid.* lxxvi. p. 163 (1925).



the variation of the susceptibility of the diamagnetic gases  $H_2$ ,  $N_2$ , and  $CO_2$  with change of pressure \*, point, though with considerably less certainty, to the orientation of molecules in the field.

It seemed reasonable to suppose that certain optical effects might follow from the presence of such orientation. Suppose, for example, that light is passed through a gas composed of single-quantum atoms all orientated in the direction of a uniform magnetic field, the path of the beam being parallel to the direction of the field; then the electric vector will lie always in the invariable plane of the atoms. When, however, the same atoms are orientated at random, that is, when no field is present, the direction of the electric vector can bear no particular relation to the orbital planes. It seems reasonable to suppose that the polarization of the atoms induced by the light is not the same in the two cases; and hence a difference in *refractive index* of the gas with and without the presence of the magnetic field might conceivably be expected.

The experiments to be described were undertaken with a view to detecting such an effect.

### *Experimental Arrangements.*

The apparatus employed was a Jamin interferometer, one tube of which contained the substance under examination, the other being evacuated. The tubes were surrounded for their whole length by an air core solenoid. A shift of the interference fringes on throwing on the field was looked for.

The wave-length employed was uniformly the mercury green. Light from a quartz mercury arc, suitably filtered, was focussed on the slit of a collimator, the lens of which was furnished with a diaphragm 1.5 cm. in diameter. The collimated beam then fell on the first of the Jamin mirrors, which were supplied by Hilger. The tubes, being intended for the examination of sodium, were of steel: being 100 cm. long, 1.5 cm. in diameter, and closed with worked glass disks supplied by Hilger. Iron or steel was rigidly excluded from the rest of the apparatus. The interference fringes were viewed in a telescope furnished with an ocular micrometer. The breadth of the fringes was 3 scale divisions; further broadening caused the edges to become unduly blurred. A movement of a thirtieth of a fringe could readily be detected.

\* Glaser, *Ann. Phys.* lxxv. p. 459 (1924).

It was essential to have the fringes exceedingly steady, so that a given line of the ocular scale could be brought on to the edge of one of the fringes and held there until the field was thrown on. Special precautions were taken therefore to eliminate vibration. The apparatus was supported on a heavy slate slab which rested on a concrete pier built solid with the concrete floor in the basement of the building. The Jamin mirrors and the tubes were supported on heavy brass castings, the bases of which were hand-scraped flat to a surface-plate before being bolted down on the slate. All work was done at night and trouble from vibration was entirely absent.

With a current of 25 amps. in the solenoid, the field inside the steel tubes, as measured with search-coil and fluxmeter, was 184 gauss. The tubes were carefully demagnetized before each observation.

*Experiments with  $H_2$ ,  $O_2$ ,  $N_2$ ,  $CO_2$ .*

It is essential that the pressures under which the gases are examined should not be too high, it being necessary that the period of the Larmor precession should be at least of the same order as the mean time between collisions. Otherwise it appears that, in accordance with the periodicity condition, space quantization is not sharply defined. With the fields employed, pressures higher than 1 cm. are to be avoided.

In examining the above gases, both tubes were evacuated to .001 mm., and the gas to be examined admitted to one of them up to a pressure of .6 to .8 cm. The entrance of the gases caused a shift of some six to eight fringes with the apparatus used, so that reading to a thirtieth of a fringe, a change of half a per cent. in the refractive index, due to the magnetic field, would have been observable.

Preliminary experiments were made with dry air, and a null result obtained.

$H_2$  and  $O_2$ , prepared by the electrolysis of carbonate free sodium hydroxide;  $N_2$  from the air, oxygen being absorbed by alkaline pyrogallol,  $CO_2$  by potassium hydroxide;  $CO_2$  from pure marble and hydrochloric acid, were examined. The gases were dried over phosphorus pentoxide before being admitted to the apparatus. Three independent observations were made on each gas. In each case, the effect of introducing a Nicol in the path of the illuminating beam was tested. The prism was orientated to give plane polarized light with the electric vector vertical; the gases were contained in the tube receiving light from the face of the first

Jamin mirror, to avoid the ellipticity introduced by reflexion from the silvered back of the mirror.

Uniformly null results were obtained \*.

### *Sodium.*

It might be, as Pauli has pointed out in a discussion of Glaser's results †, that the number of possible orientations for the molecules of the gases examined is so great that no distinction can safely be drawn between quantum and classical diffuse orientation. Such a possibility is excluded in the case of sodium, which, as an alkali metal, may reasonably be supposed to possess a single quantum atom, orientating with its axis in the direction of a uniform field. The conditions for observing any possible alteration in the refractive index are therefore favourable for sodium.

For the experiments with sodium the ends of the tubes were cooled by means of water-jackets, and both were heated between the water-jackets by an electric furnace. The open ends of the solenoid were packed around the water-jackets with cotton-wool, and the furnace lagged with asbestos. Mirage was very slight.

The sodium, freed from naphtha by distillation, was introduced into one of the tubes, which was immediately evacuated and heated to a temperature of  $500^{\circ}\text{C}$ . It was maintained at this temperature for five or six hours, the pump being in operation throughout. Pumping was continued until the McLeod gauge showed less than  $\cdot 01$  mm. Observations were taken in a temperature range of  $475^{\circ}$ – $410^{\circ}\text{C}$ ., the apparatus being continuously evacuated during the experiments.

Vapour pressures of the alkali metals are difficult to measure, and the agreement between independent observations leaves much to be desired. Accepting the recent determinations of Rodebush and de Vries ‡, interpolation gives a pressure range of  $2\cdot 5$ – $0\cdot 5$  mm. for sodium vapour

\* The present experiments on  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$  confirm similar observations on  $\text{H}_2$ ,  $\text{O}_2$ , and He, made in the Cavendish Laboratory by Mr. H. W. B. Skinner, who has very kindly communicated his results to me. Skinner, using a sodium flame as source, finds that a transverse magnetic field of some 10,000 gauss has no effect on the refractive index for pressures varying from 0–760 mm. He has also established the absence of double refraction independent of the field strength for  $\text{H}_2$ ,  $\text{O}_2$ , and He, within the same pressure range.

† *Phys. Zeit.* xxvi. p. 212 (1925).

‡ Rodebush and de Vries, *Journ. Amer. Chem. Soc.* xlvii. p. 2488 (1925).

between  $475^{\circ}$  and  $410^{\circ}$  C. On heating to  $475^{\circ}$  six fringes moved across the reference line of the ocular. The furnace was switched off, and observations were taken as successive fringes returned to the reference line as the vapour cooled. Two experiments were made with sodium, in each case with illumination by ordinary and plane polarized light. Null results were obtained \*.

### *Discussion.*

The absence of any observable change in the refractive index when the field was thrown on indicates that within the limits of observation the atoms and molecules examined react to light in a manner independent of their orientation—in short, that they behave as if they were optically isotropic.

Isotropic behaviour of this kind is of considerable theoretical interest, presenting as it does in a slightly different aspect an anomaly in the theory of space quantization which seems to need further investigation. Stern † first pointed out that anisotropy, resulting in a magnetic double refraction independent of the field strength, appeared to follow as a necessary consequence of the theory ‡. Its absence in sodium vapour was demonstrated by Gerlach and Schütz §, for the immediate neighbourhood of the D lines; while the present observation on sodium is for a region well removed from the D lines. After the experiments described here were in progress, Heisenberg || pointed out that the absence of double refraction independent of the field strength is connected formally with the assumed absence of total polarization in a Zeeman multiplet; a beginning towards accurate intensity measurements of Zeeman components is, however, only now being made, chiefly by Ornstein and his co-workers in Utrecht. Again, Heisenberg's conclusion strictly applies, apparently, only to those absorption lines which show a normal triplet; nevertheless, it would be of interest to decide whether

\* Recent experiments on the breadths of absorption lines of Na vapour (Harrison and Slater, *Phys. Rev.* xxvi. p. 176, 1925), indicate the presence of diatomic molecules in appreciable numbers above  $450^{\circ}$ . The recognition of this factor makes the present observation on Na rather less unequivocal than appeared at first.

† Stern, *Zeit. für Phys.* vii. p. 617 (1922).

‡ Magnetic double refraction, influenced by the field strength, in the neighbourhood of an absorption line (Voigt-Wiechert double refraction) is, of course, well known, and due to well recognized factors.

§ Gerlach and Schütz, *Naturwiss.* xi. p. 637 (1923). See also footnote above.

|| Heisenberg, *Zeit. f. Phys.* xxxi. p. 617 (1925).

a substance will show anisotropic behaviour in the region where an intermediate stage of the Paschen-Back effect is displayed by one of its absorption lines.

I am glad of this opportunity to express my gratitude to Professor G. P. Thomson for much helpful discussion. I am indebted to Mr. C. G. Fraser, instrument maker in the Department, for invaluable technical assistance.

LXXVIII. *On Entropy of Radiation. II.* By MEGHNAD SAHA and RAMANI KANTO SUR, *Physics Department, Allahabad University, India* \*.

IN a previous paper, it has been shown that the thermodynamical probability of a system is given by the law

$$W = \{\gamma\} / \{\gamma\}_0. \quad (1)$$

Where  $\{\gamma\}$  = phase-space described by the system at temperature  $T_0$ ,  $\{\gamma\}_0$  = phase-space described at absolute zero. It was shown that the absolute value of entropy of perfect gases could be deduced from this theorem.

The same formula can be applied for deducing the entropy of radiation. Since the time when Bartoli deduced the existence of radiation pressure from thermodynamical reasoning, it has been customary to look upon radiation as a sort of perfect gas. But the analogy is often misleading, for the energy of gaseous molecules is capable of continuous variation, while according to Planck, radiant energy or energy of light pulses can vary only in multiples of  $h\nu$ . If  $E_\nu$  = total energy of frequency  $\nu$ , then

$$E_\nu = N_\nu \cdot h\nu \quad (2)$$

$N_\nu$  = number of energy elements.

In calculating the probability, we have further to find out the number of ways in which a quantum can be contained within unit volume. This is equal to  $A = \frac{8\pi\nu^2}{c^3}$ . The deduction of this theorem forms the greatest difficulty in the theory of black body radiation. In the original method of deduction by Jeans and others,  $\frac{8\pi\nu^2}{c^3}$  represents the total number of stationary waves in unit volume having their

\* Communicated by the Authors.

frequency between  $\nu$  and  $\nu+1$ . It is deduced in a most complicated way from electromagnetic considerations.

Bose has recently given a very elegant and simple method of deducing the theorem

$$A = \frac{8\pi\nu^2}{c^3}, \quad . . . . . (3)$$

which is reproduced here.

According to modern conceptions, a pulse of light carries with it the momentum  $\frac{h\nu}{c}$  in the direction of its motion. It has got the components

$$p_x, p_y, p_z, \text{ where } p_x^2 + p_y^2 + p_z^2 = \frac{h^2\nu^2}{c^2}.$$

The phase-space described by the pulse in its translatory motion is, according to Planck,

$$. . . \int dp dq . . . = \dots \int_0^{\nu+1} dx dy dz dp_x dp_y dp_z = \frac{4\pi h^3 \nu^2}{c^3} V. \quad (4)$$

According to the quantum theory, the phase-space can be split up into cells each of volume  $h^3$ , hence the total number of cells

$$= \frac{4\pi h^3 \nu^2}{c^3} V / h^3 = \frac{4\pi \nu^2}{c^3} V, \text{ or } \frac{8\pi \nu^2}{c^3} V \quad . . . (5)$$

when we take both the polarized pulses. The number  $P = \frac{8\pi \nu^2}{c^3}$  represents the total number of ways in which a quantum  $h\nu$  can be contained within unit volume. The idea is therefore the same as the number of stationary waves.

The essential point in the above argument is that the *translatory motion* of a pulse of light can be treated according to the quantum theory, viz.,  $\int dp dq = h$  for any one of the degrees of freedom of the pulse of light.

We can now calculate the entropy of radiation by using the relation

$$W = \{\gamma\} / \{\gamma\}_0.$$

Now

$$\{\gamma\} = \Pi(\mu)P, \quad . . . . . (6)$$

where  $\{\mu\}$  = phase-space described by one pulse in its internal electromagnetic vibrations,  $P$  = permutability of the pulses. We are not yet acquainted with any method for expressing the internal vibrations within a light-pulse in terms of Hamiltonian coordinates. Planck and other authors, *e. g.* Darwin and Fowler, identify the pulse with some

resonator—Hertzian oscillator, or the Bohr-Vibrator. But we think it may be possible, in the case of a free pulse, to avoid this appeal to material carriers. At any rate, we assume that the pulse is subject to Hamilton's equation

$$\iint dp dq = h,$$

for each of its degrees of vibrations.

Then  $\Pi(\mu) = h^{3N\nu},$

which means that the pulses do not interchange energy, like gas-molecules, but are independent of each other.

$$P = \frac{A+N!}{A! N!} \cdot \cdot \cdot \cdot \cdot \cdot \quad (7)$$

because any one of the cells may contain  $0, 1, 2 \dots N,$  pulses.

Thus  $\{\gamma\} = h^{3N\nu} \frac{A+N!}{A! N!} \cdot \cdot \cdot \cdot \cdot \cdot \quad (8)$

We have now to find out the value of  $\{\gamma\}_0$ . This brings us to the point: how we can reach the absolute zero by using radiation as the working substance in a Carnot reversible engine as was first done by Bartoli. Wien showed that we can pass from a radiation space at temperature  $T$  to a space at temperature  $T'$  by a virtual slow displacement of the walls. The wave-lengths of radiation enclosed within the space are changed according to the relation

$$\lambda T = \lambda' T',$$

or  $\nu = \alpha T.$

Hence at  $T=0, \nu=0$ , *i. e.* at absolute zero, it is not possible to have any radiation at all.

This brings us to an interesting analogy. We have seen in the previous paper that if we use a gas as a working substance in the Carnot cycle, absolute zero can be attained only when all matter has been annihilated. The present theorem tells us that if we use radiation as a working substance, absolute zero can be attained in a space where all radiation has been completely annihilated.

We thus obtain  $A=0, P=1,$   
and  $\{\gamma\}_0 = \Pi(\mu)P = h^{3N\nu}, \cdot \cdot \cdot \cdot \cdot \cdot \quad (9)$

$$\therefore W = \{\gamma\}/\{\gamma\}_0 = \frac{A+N!}{A! N!}, \cdot \cdot \cdot \cdot \cdot \cdot \quad (10)$$

from which the value of  $S$  can be easily deduced.

If we use  $A, d\nu, N, d\nu$  instead of  $A$  and  $N$ , we obtain

$$\text{Probability } W = \frac{(A d\nu + N d\nu)!}{A d\nu! N d\nu!}.$$

It is easy to see that this equals

$$\left\{ \frac{(A_\nu + N_\nu)!}{A_\nu! N_\nu!} \right\}^{d\nu}, \quad \dots \quad (11)$$

or in other words,

$$S_\nu d\nu = d\nu \cdot \kappa \log \frac{(A_\nu + N_\nu)!}{A_\nu! N_\nu!}, \quad \dots \quad (12)$$

$S_\nu d\nu$  now denoting entropy of radiation having their frequency between  $\nu$  and  $\nu + d\nu$ .

The value of  $S_\nu$ ,  $U_\nu$  can be calculated with the aid of the above expression, and the relation  $\frac{dS_\nu}{dU_\nu} = \frac{1}{T}$ , but as these calculations are to be found in every standard text-book on radiation, they are not reproduced here.

### LXXIX. *Notices respecting New Books.*

*The Surface-History of the Earth.* By JOHN JOLY, Sc.D., F.R.S., Fellow of Trinity College, Dublin. (Oxford University Press. Royal 8vo. 192 pages, 13 plates, 11 figures, and an Oro-Bathymographical Chart of the World. 8s. 6d. net.)

**I**N this well printed and illustrated book Professor Joly puts forward a theory of the past history of the earth which differs materially from the one generally accepted. As the earth after its ejection from the sun gradually cooled a solid crust was first formed on the surface where gravitational forces had placed the liquid constituents of least density. The contraction which generally accompanies solidification might lead to the sinking of the material first solidified, but eventually a continuous solid crust would be formed which would be supported hydrostatically by the liquid or semi-liquid beneath it. This theory of the hydrostatic support of the solid crust and its consequences is known as Isostasy. The absence of internal tides and the presence of seismic waves lead to the conclusion that the earth is now solid, and as its still hot interior cools and therefore contracts the outer shell has to shrink like the skin of a drying apple and does so, producing at intervals earthquakes and at times geological revolutions. It is on the origin of these revolutions that Professor Joly differs from the above outline. He believes that the radioactive material in the earth's crust is more than sufficient to supply the heat lost from its surface and the surplus heat accumulates in a layer about 70 miles below the surface. The rock in this layer slowly melts, expanding as it does so and exerting pressure on the crust above it. The crust at times gives way producing earthquakes and geological revolutions as under the former theory. The shrinkage theory provides an explanation of the phenomena so long as there is loss of heat by the interior, the bursting theory provides it so long as radioactive material is present in sufficient quantity. There are, however, several difficulties to be overcome before the new theory can be accepted



as satisfactory. One of these is the concentration of the surplus heat from radioactive changes in a particular layer, and another the secular rise of temperature of the earth during the whole of its past history owing to the amount of radioactive material postulated. The author unfortunately bases his calculations of the expansion on melting of the rocks 70 miles below the surface on the 10 per cent. increase of volume found when rocks melt at atmospheric pressure. Since a pressure of 12,000 atmospheres is known to reduce the volume increase of a solid on melting to less than half its value at atmospheric pressure, a serious revision of these calculations is necessary.

While the book cannot be said to establish the theory which it advances, it is thoroughly stimulating and will result in a more careful and complete examination of the problems which the physical history of the earth presents.

C. H. LEES.

*The Electron.* By R. A. MILLIKAN. Second Edition. (University of Chicago Press. Price 9s. 6d.)

*A System of Physical Chemistry.* Vol. II. *Thermodynamics.* By W. G. McM. LEWIS. Fourth Edition. (Longmans. Price 15s.)

*Exercises in Practical Physics.* By Sir A. SCHUSTER and C. H. LEES. Fifth Edition. (Cambridge University Press. Price 12s. 6d.)

THE three books cited above have little in common except that their excellence, each in its particular field, has led to repeated calls for new printings, for, while Professor Millikan's book is ostensibly only in its second edition, it has already gone through eleven impressions. Since it may be assumed that they are already familiar to most readers of the *Philosophical Magazine*, it is necessary to do little but indicate the changes made in the latest edition as compared with the previous one; and, since in the case of the two latter books these changes are comparatively slight, the books have been placed together.

Professor Millikan's first edition was published in 1917, and on account of the rapid advances in some of the subjects which he handles, there has been a certain amount of completely new matter to incorporate. There is a brief reference to Aston's work on isotopes (not indexed, by the way). Bohr's periodic  $n_k$  scheme is described, with the well-known diagrams of atomic structure of typical atoms first published by Kramers. Many other pieces of recent work have been embodied in the last two chapters, which deal respectively with the Structure of the Atom and the Nature of Radiant Energy. Among these may be mentioned C. D. Ellis's work on the nuclear  $\gamma$  rays, the collisions of the second kind of Klein and Rosseland, and the intriguing Compton effect, the last-named being illustrated by a plate reproducing an excellent photograph showing the displaced lines. The work of the author and Bowen on the spectra of multiply ionized atoms is all too briefly noted. All these features of recent research are described with the conciseness and clarity which are so marked a feature of the book as a whole. Professor Millikan needs no recommendation to the readers of this Magazine, and so the reviewer will spare them a eulogy.

Professor W. C. McC. Lewis has added to his book an account of G. N. Lewis's treatment of solutions, as described in G. N. Lewis and Randall's 'Thermodynamics,' and of one or two other recent investigations in chemical thermodynamics.

Sir Arthur Schuster and Professor C. H. Lees have replaced some of their simpler experiments by somewhat more advanced ones. The book, it will be remembered, is designed to cover adequately all the experimental work required for a pass degree, and the standard demanded seems to be advancing. These two books are so well known that no more need be said.

*Mémoires des Sciences Mathématiques.*

1. *Sur une forme générale des équations de la dynamique.* By PAUL APPELL.
2. *Fonctions entières et fonctions méromorphes.* By G. VALIRON.
3. *Séries hypergéométriques de plusieurs variables, polynômes d'Hermite et autres fonctions sphériques de l'hyperespace.* By PAUL APPELL. (Gauthier-Villars. Price 10 francs each.)

THESE booklets are the first three of a series, to comprise about one hundred small volumes, written by eminent Continental mathematicians, and published under the auspices of many leading mathematical societies. The aim of the series is to deal with theories of modern mathematics so as to appeal to the research student, and also to the professed mathematician who desires an acquaintance with the present position, and possibilities, of branches of the science outside his own range of work. Each volume is to contain a short introduction to its subject, a detailed description of the main theorems already acquired and indications of probable lines of future research, ending with a sufficient bibliography.

Outlines of proofs and methods special to the subject will be included in the scope of most of the volumes, but critical comparison of alternative methods will not be introduced. Such a collection should then occupy a position between the general treatise and the encyclopædia; but the exact position may well be lacking in definiteness unless the general editor be given wide powers, and exercise his functions extensively. Detailed discussion of elementary problems in illustration of general theorems, on the one hand, and, on the other, austere lists of theorems without discussion or interconnecting matter are both possible dangers.

The three volumes under review show that these and, doubtless other dangers have been successfully avoided, and within the limits of fifty to seventy pages are comprised clear and readable accounts of the theories considered. The first volume deals with Appell's own method of forming the equations of dynamics by means of the "energy of accelerations,"

$$\sum \frac{1}{2} m (\ddot{x}^2 + \ddot{y}^2 + \ddot{z}^2),$$

whilst the contents of the others are sufficiently described by their titles. No very serious misprints have been noticed.

LXXX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 704.]

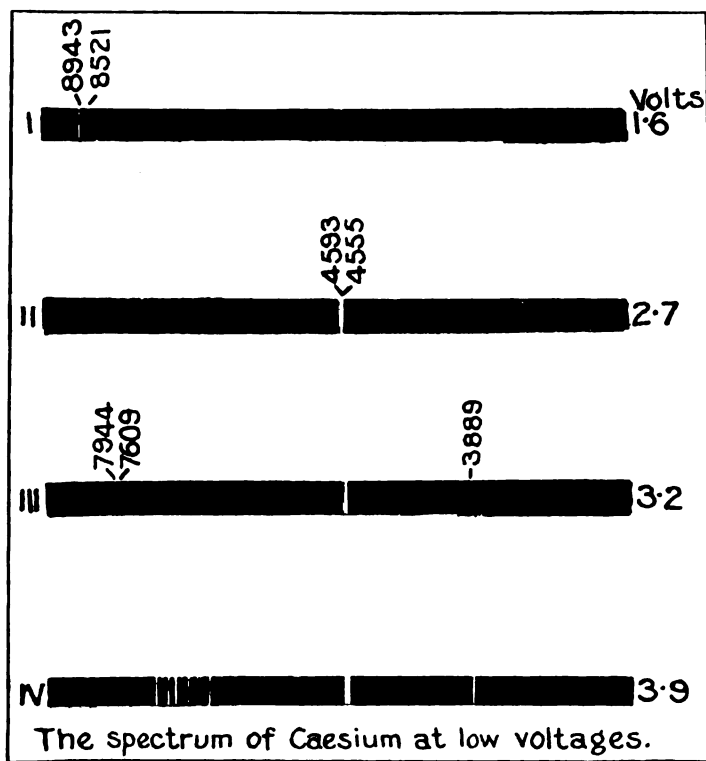
December 2nd, 1925.—Dr. J. W. Evans, C.B.E., F.R.S.,  
President, in the Chair.

THE following communication was read :—

‘The Depth of Origin of Earthquakes.’ By Richard Dixon  
Oldham, F.R.S., F.G.S.

Methods of determining the depth of origin of an earthquake, dependent on observations of the time of occurrence, demand records of a degree of precision, and in numbers, which are seldom available. The same objection applies to the Dutton method, based on variation in the intensity of shock; but the method is capable of a simplification which will make it applicable to any case where the area affected by the sensible shock, and the maximum degree of violence attained, can be determined. The original method has been examined, and it is shown that, although the method is sound in principle, two important errors have been introduced in the application. Acceleration has been taken as the measure of intensity, whereas the formula demands that the product of maximum acceleration and amplitude of displacement should be used; and the effect of absorption of energy in transmission has been treated as negligible. It is shown that either of the errors so introduced would be material, but, being opposite in sign and about equal in amount, they nearly neutralize each other, with the result that the depth obtained is approximately correct. The simplified method is applied to the discussion of the Italian record for the years 1897–1910, comprising 5605 distinct shocks, it is found that more than 90 per cent. of these originated at depths of less than 10 km., and mostly round about 5 km.; while only 1 per cent. originated at depths exceeding 30 km. This is in strong contrast with the depths of origin of the distant records, which have been computed by different workers at figures ranging from 50 km., in a few cases, to, in most cases, 100 km. or more. From this it is concluded that the ordinary local earthquake, which can be felt, differs from that which gives rise to distant records, not merely in magnitude, but also in character of cause and origin: in those cases where distant records accompany a destructive earthquake the disturbance has a twofold origin, the episeism, or surface-shock, by which the damage is directly caused, being a secondary result of the bathyseism, which is the origin of the distant record. The great number of local shocks are purely episeisms, without any recognizable bathyseism; in rare instances the sensible shock appears to have originated directly from the bathyseism, unaccompanied by any recognizable episeism.

[The Editors do not hold themselves responsible for the  
views expressed by their correspondents.]





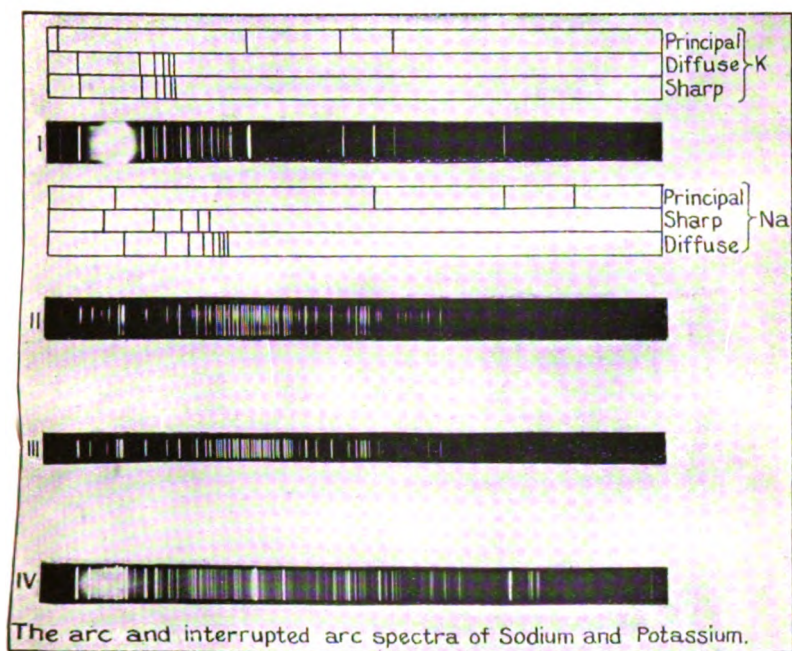
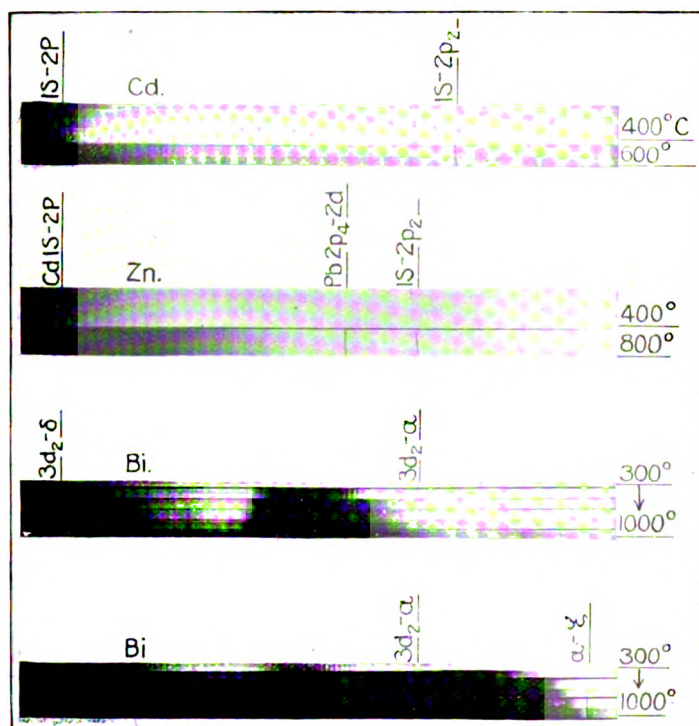




FIG. 2.







S



Tuning-fork

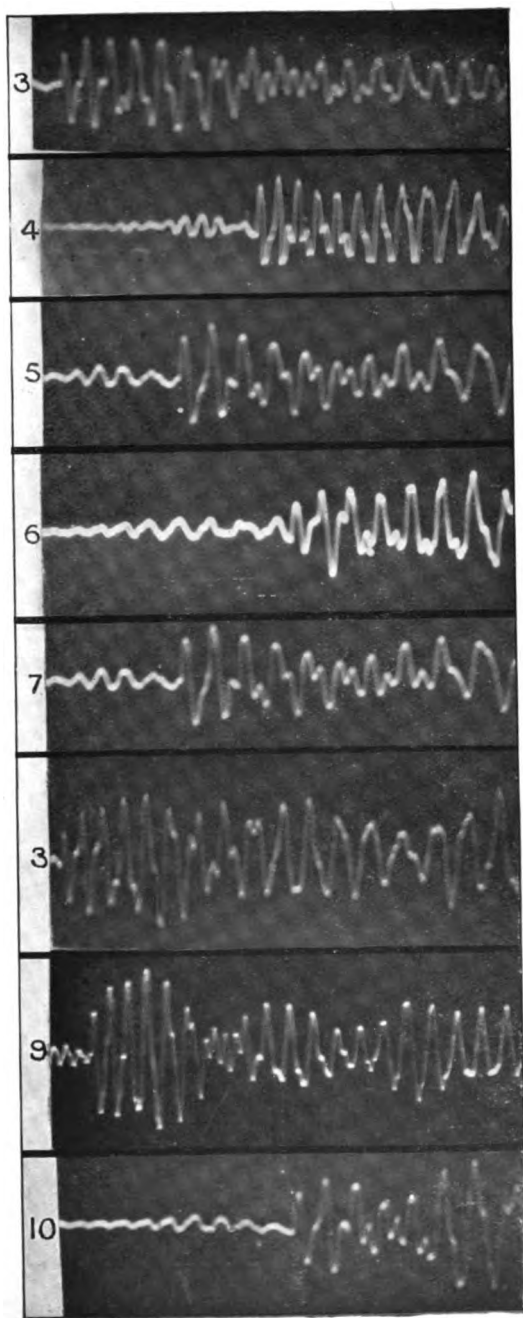


FIG. 2 b.

FIG. 3 *c.*

FIG. 5.







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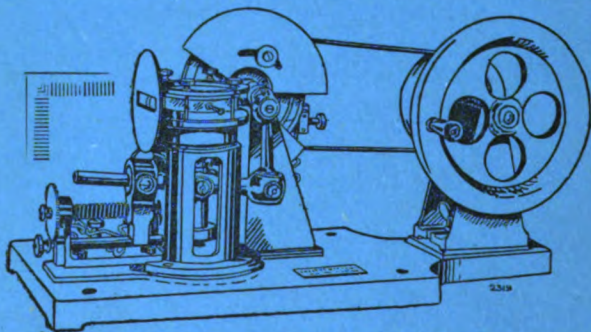
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MAY 1926.

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LXXXI. *The Intensity of Reflexion of X-Rays by Crystals.*  
*By W. LAWRENCE BRAGG, F.R.S., Professor of Physics, Manchester University ; C. G. DARWIN, F.R.S., Professor of Mathematical Physics, Edinburgh University ; and R. W. JAMES, Senior Lecturer in Physics, Manchester University\*.*

THE paper is a general review of formulæ that describe the intensity of the reflexion of X-rays from crystals.

Two formulæ have been used, one applicable to perfect crystals, the other to a mosaic of small fragments. The main object is to determine the scattering of radiation by the atom, and it is necessary to know which formula is applicable.

Numerical comparison shows that rock-salt, fluorspar, and barytes approximate closely to the imperfect type, while calcite is intermediate.

Various corrections are discussed which must be applied to crystals of intermediate character.

---

1. INTRODUCTION.

THE authors were privileged recently to attend a conference, organized by Prof. P. P. Ewald, of the Technische Hochschule of Stuttgart, at which the question of intensity of X-ray reflexion was the chief subject of discussion. The members of the conference were P. P. Ewald,

---

\* Communicated by Prof. W. L. Bragg.

M. v. Laue, L. Brillouin, R. W. G. Wyckoff, H. Mark, I. Waller, A. D. Fokker, P. Debye, K. Herzfeld, H. Ott, and ourselves, and it was held at Holzhausen, on the Ammersee, in Bavaria, in September 1925. We wish to take this opportunity of recording our gratitude to Prof. Ewald for having arranged the conference. It afforded a unique opportunity of exchanging views, and was the greatest inspiration for future work.

The subject of intensity of reflexion has been dealt with by us in several theoretical and experimental papers. The present review of our work, and amplification of certain parts of it, is a direct result of the conference, where the aspects of the subject in which we are particularly interested were very fully discussed. It is impossible to assign credit for some of the ideas which arose in the discussion, and we must rest content with a general acknowledgment to all the other members. One fact which emerged as a result of the discussion was that certain points in our previous papers had suffered in clearness through an attempt to put them concisely, and part of the present paper is devoted to expanding these arguments into a more intelligible form.

Renewed interest in the whole question of intensity of reflexion has been recently excited by the elegant analysis due to Prof. Ewald\*. He has treated the problem of reflexion by a perfect crystal, and has placed on a sound mathematical basis the interaction of the X-ray waves and an organised array of atoms. This has raised the question of how far actual crystals conform to this standard, which it is our chief aim to discuss here.

*Note.*—The following are the chief papers of our own in chronological order to which we shall refer by abbreviated titles. We may also here give the meanings of some of the chief symbols used in them, especially as the notation was not quite uniform:—

Darwin, <i>Phil. Mag.</i> vol. xxvii. p. 315, 1914 .....	D I.
" " " " vol. xxvii. p. 675, 1914 .....	D II.
Bragg, James, & Bosanquet, <i>Phil. Mag.</i> vol. xli. p. 309, 1921...	BJB I.
" " " " " " vol. xlii. p. 1, 1921 ...	BJB II.
" " " " " " vol. xlii. p. 433, 1922.	BJB III.
Darwin, <i>Phil. Mag.</i> vol. xliii. p. 800, 1922 .....	D III.

The following symbols are common to all:—

Wave-length .....	$\lambda$
Linear absorption coefficient .....	$\mu$
Number of lattice units per c.c. ....	$N$

\* Ewald, *Phys. Zeitschr.* vol. xxvi. pp. 29–32 (1925).

The following are divergent :—

	D I, II.	BJB I, II.	D III.	Here.
Angle of reflexion.....	$\phi$	$\theta$	$\theta$	$\theta$
Arbitrary angle of setting ...	$\theta$	$\theta + \epsilon$	$\theta + u$	$\theta + u$
Amplitude of wave scattered by an atom at angle $2\theta$	$\left\{ f(2\theta, \lambda) \left[ \frac{e^2}{mc^2} F(2\theta, \lambda) \right] \left[ f(2\theta, \lambda) \right] \left[ \frac{e^2}{mc^2} F(2\theta, \lambda) \right] \right\}$			
Integrated reflexion .....	...	$E\omega/I$	$\rho$	$\rho$
Distance between successive planes of lattice	$a$	$d$	$a$	$a$

The advantage of using  $F$  instead of  $f$  is that it is dimensionally a pure number, and equal to unity for a single electron.

We may also here note certain derived quantities that play an important part in the work.

The amplitude of the wave scattered by a single plane is

$$q = N \frac{e^2}{mc^2} \cdot \frac{F\lambda a}{\sin \theta}.$$

The quantity actually measured in imperfect crystals is

$$Q = \left( N \frac{e^2}{mc^2} F \right)^2 \frac{\lambda^3}{\sin 2\theta}.$$

## 2. TWO FORMULÆ FOR INTENSITY OF REFLEXION.

The question of the intensity of X-ray reflexion is full of difficulties. Any mathematical expression calculated to give the relationship between incident and reflected energy of radiation for a definite experimental disposition contains a number of factors which need to be evaluated. The three factors which are of especial importance depend on

- (a) The amplitude of the wave scattered by each individual atom of the crystal, for definite directions of incident and scattered beam.
- (b) The effect of the heat motion of the atoms, giving rise to the temperature factor which reduces the intensity of reflexion as the temperature of the crystal is raised. The existence of this factor\* was originally pointed out by Debye, and its effect was first observed by Sir W. H. Bragg.
- † (c) The interaction of the waves scattered by the atoms of the crystal which are in a more or less orderly arrangement.

\* *Verh. deutsch. Phys. Ges.* xv. pp. 678, 738, and 867.

In order to make any advance, the last of these factors must be satisfactorily evaluated. If this can be done, there is hope of a direct determination of the second factor by experimental measurements at different temperatures, and so of a determination of the first factor by measuring the intensity of reflexion from a number of types of crystal.

The reward of accurate results is great, since they will yield more direct information as to the positions of the electrons in the atom than is obtainable by any other methods. This must be regarded as the main objective, but a knowledge of the scattering powers of the atoms is also essential to the application of X-rays to discover the structure of complex crystals. After fifteen years of crystal analysis we are not in possession of a means of utilizing to the full the very accurate intensity measurements which can easily be made, and have to be content with qualitative tests. All who have worked in this field will appreciate the unsatisfactory nature of the arguments on which analyses are based.

The difficulty in the mathematical calculation of the last factor arises from the nature of the crystals with which we have to work. On the one hand, an orderly arrangement of atoms is present, since all the X-ray diffraction effects arise from such an arrangement. The accurate comparative measurements of X-ray wave-lengths, extending to five significant figures, show that the atoms in a crystal are arrayed in a very perfect manner. On the other hand, it is clear from experimental results that this perfection has its limits. The orderly arrangement does not extend over the whole volume of the crystal from which the reflected radiation originates, and calculations based on the supposition of an absolutely perfect crystal lead to results which are at variance with experiment. There is no question here of a small correction to be applied on account of the imperfection of the crystal. The observed intensity of reflexion may be from ten to fifty times as great as that given by calculations. This shows the necessity of taking into account the actual nature of the crystal, and the caution with which calculations must be applied.

It will simplify the discussion to consider two extreme cases of crystalline arrangement. Some kind of regular arrangement must, of course, be postulated in order that diffraction effects may be observed. On the one hand, a crystal may be regarded as a *mosaic* composed of small crystalline fragments which are approximately parallel to each other, but whose orientations are distributed through

an angular range of many minutes of arc on either side of a mean direction. All atoms within each fragment are regarded as being in perfect arrangement. The number of atoms in each fragment is so small that their effect on each other when diffracting radiation may be neglected. This is the extreme case of an imperfect crystal, and may be termed the *ideally imperfect crystal*, or *mosaic crystal*. A very simple mathematical expression gives the intensity of the diffracted radiation. Experimental results seem to show that many crystals do in fact approach this ideal type of imperfection. Calculation shows that the homogeneous fragments must not be more than a few thousand atomic planes in depth in order that the mathematical expression may be valid.

On the other hand, we may suppose the crystal to be absolutely perfect. The physical significance of this statement can also be analysed. It means that the small homogeneous fragments of crystal are arranged so regularly that their orientations do not vary by more than a fraction of a second of arc. An entirely different mathematical formula, but one which is again of a very simple type, applies to the diffraction of X-rays by such a crystal. The intensity of reflexion calculated by the second formula is only a fraction of that calculated by the first formula. Experiment has not yet indicated that this ideal perfection is realized in actual crystals. It appears to be the case that all crystals are neither ideally perfect nor ideally imperfect, but have a structure which lies between the two extremes, and in most cases much closer to the ideally imperfect.

As far as we are aware, the expressions for these two cases were first given by one of us in 1914 in the papers D (I) and D (II). In order to give the expression a precise form which may be used for quantitative work the experimental arrangements must be defined. At the date of those papers it was usual to work without slits so that the whole spherical wave fell on the face of a fixed crystal. Some part of this would be at the proper angle, and the sheet of radiation would be effectually limited only by the *length* of the slit of the ionization chamber. This method has proved not so convenient in practice as another due to Sir W. H. Bragg. Here the incident beam is defined by slits, so as to be approximately parallel, and the crystal is rotated with constant angular velocity through the settings for which reflexion occurs. It is obvious that there is a very close relationship between the methods, since in each the crystal is equally exposed to radiation at all angles near the angle of reflexion—in the first

because of the divergency of the incident beam, and in the second because of the uniform rotation of the crystal. In consequence of this it is very simple to translate the formulæ of D (I) and D (II) into the corresponding expressions for the other method, and the latter have the advantage of not containing such quantities as the length of the slit and the distance from source to observing-chamber. In quoting these formulæ we shall express them in the second form without further explanation.

The amount of the reflexion is experimentally described by means of the "Integrated Reflexion," which is measured in the following way. If  $\theta$  is the angle of reflexion, at near settings of the crystal there will be a certain amount of radiation reflected, and its effect in the observing-chamber will be proportional to the time the crystal is so set. Thus, if we observe that on turning right through the region of reflexion the energy obtained is  $E$ , we must expect that the reflexion will be measured by  $E\omega$ , where  $\omega$  is the angular velocity of turning. It was in fact observed by Sir W. H. Bragg\* that this quantity was constant for different specimens of a crystal although the width of the region of perceptible reflexion varied widely. The quantity  $E\omega$  is to be compared with  $I$ , the energy produced by the incident beam in the observing-chamber in one second. The ratio  $E\omega/I$  or  $\rho$  is the integrated reflexion. It is of no physical dimensions, and has the great advantage over the quantities worked out in D (I) and (II) that it is independent of the sizes of slits and all the purely geometrical features of the experiment.

It is in some ways convenient to interpret  $\rho$  as follows. Conceive that the radiation was perfectly reflected when it struck the crystal within a given range of angles, and was not reflected at all outside this range. As the crystal rotates with an angular velocity  $\omega$ , it reflects the incident radiation  $I$  for a short time  $t$ . The total amount reflected,  $E$ , will be equal to  $It$ , so that  $\frac{E}{I}$  measures the time  $t$ , and  $\frac{E\omega}{I}$  measures the angular range  $\omega t$  over which total reflexion takes place. The integrated reflexion  $\rho$  is thus the angular breadth of this region (in circular measure). This way of regarding the matter has a very direct application to the case of the perfect crystal.

\* W. H. Bragg, *Phil. Mag.* xxvii, p. 881 (1914).

The formula of D (I), p. 322 (suitably modified), is

$$\rho = \frac{Q}{2\mu} = \left( N \frac{e^2}{mc^2} F \right)^2 \lambda^3 / 2\mu \sin 2\theta. \quad (1)$$

The temperature factor  $e^{-B(T) \sin^2 \theta}$  and polarization factor  $\frac{1 + \cos^2 2\theta}{2}$  are omitted, and a lattice of only one type of atom is here being used.

The formula (1) was originally worked out on the assumptions which Laue made when he first calculated the diffraction of a crystal; that is to say, the crystal was assumed perfect, but all interactions between the waves scattered by the atoms were neglected. The work, however, itself showed that these assumptions were inadequate (the argument is outlined in § 8 below), and it was conjectured in D (II) that it was actually the correct formula to apply to an ideally imperfect crystal. This was proved in BJB I. However, it is shown in D (I), p. 331, that this formula gives a reasonable value for the ratio between incident and reflected radiation for rock-salt. Moseley and Darwin\* measured this ratio under definite experimental conditions, using white radiation. The value obtained agrees with the formula if the average effective number of electrons in sodium and chlorine is about ten, which is of the right order. The applicability of the formula has been confirmed by Compton† and Bragg, James and Bosanquet using monochromatic radiation and a rock-salt crystal (BJB I, II). We have extended the investigation to several other crystals as described below.

Formula (1) applies to the case of the ideally imperfect crystal. In order that a crystal may be considered to be of this type, its homogeneous fragments must be less than a certain size. They must be so small that the effect on any atom of the waves scattered by others in the fragment is negligible. Even when this is the case, an effect we have called "secondary extinction" modifies the formula; but this effect is amenable to experimental measurement, and will be dealt with later in this paper.

In D (II) a formula is deduced for the reflexion from a crystal which is absolutely perfect. At any depth in the crystal there exists a wave proceeding in the direction of the incident wave‡, and a reflected wave. As each crystal

\* Phil. Mag. xxvi. p. 210 (1913).

† A. H. Compton, Phys. Rev. ix. p. 1 (1917).

‡ The direction is really slightly modified by the refractive index of the crystal.



plane is crossed, the incident wave is partly reflected and modifies the amplitude of the main reflected wave, and this latter is partly reflected and modifies the incident wave. A set of difference equations is solved to obtain the final result. The amplitude of reflexion is shown to rise as the mean angle of reflexion  $\theta$  is approached. When the glancing angle is equal to  $\theta - s$ ,  $s$  being a small angle of the order of a second, reflexion becomes perfect and remains perfect till it is equal to  $\theta + s$ . After that point it rapidly diminishes. In this

$$s = q\lambda/2\pi a \cos \theta = N \frac{e^2}{mc^2} F \lambda^2 / \pi \sin 2\theta . \quad (2)$$

The expressions for the amplitude of reflexion in the three regions are given on p. 680, D (II).

Considering only the region of total reflexion, we get at once an expression for the integrated reflexion from a perfect crystal, for we have seen above that it is numerically equal to the angle  $2s$ . It is shown on p. 682, D (II), that this region contributes  $\frac{3}{4}$  of the integrated reflexion, and that the regions on either side contribute the remainder. From this it follows that the total integrated reflexion is given by

$$\rho = \frac{8s}{3},$$

and substituting for  $s$ ,

$$\rho = \frac{8}{3\pi} N \frac{c^2}{mc^2} F(2\theta, \lambda) \lambda^2 \frac{1}{\sin 2\theta} . \quad (3)$$

This expression must be multiplied by a temperature factor  $e^{-\frac{1}{2} B(T) \sin^2 \theta}$  and polarization factor  $\frac{1 + |\cos 2\theta|}{2}$ . Contrasting (1) and (3), it will be seen that certain factors in (3) are raised to the second power in (1).

### 3. PROPORTIONALITY OF INTENSITY WITH STRUCTURE-AMPLITUDE OR WITH SQUARE OF STRUCTURE-AMPLITUDE.

One of the most striking differences between these two formulæ is the following. In (3) the integrated reflexion is proportional to the amplitude reflected by a single plane of atoms in the crystal, in (1) it is proportional to the square of the amplitude. It is customary to make the latter assumption. Should we not rather expect it to be proportional to the structure amplitude itself?

In the recent paper referred to above, Ewald has raised

this question. He has obtained formulæ for the reflexion from a perfect crystal which agree with that given in D (II). They are, however, based on a more rigorous mathematical investigation carried out in a very elegant manner. He arrives at the result that about 80 per cent. of the integrated reflexion occurs in the region of total reflexion, as compared with the 75 per cent. calculated in D (II). Otherwise the formulæ are identical. At the recent conference, formula (3) was confirmed by I. Waller, who had independently evaluated the integral and arrived at the same factor of 75 per cent.

Ewald quotes cases where measurements of integrated reflexions indicate that they are proportional to structure amplitude rather than to the square of this quantity. He concludes: "Im Gegensatz zu der üblichen Auffassung ergibt sich die Intensität, so weit sie von der Totalreflexion herrührt, proportional zum Betrag der Strukturamplitude selbst nicht zu deren Quadrat."

Ewald points out the manner in which the structure amplitude influences the intensity of reflexion. Whatever the value of the structure-amplitude, reflexion is perfect over a finite range of angle. The breadth of the range, however, is proportional to the structure-amplitude, and so the effect of crystal structure on the relative intensity of spectra arises. This result follows directly from formula (2) above where  $s$  is proportional to  $q$ , the fraction of radiation reflected at a single crystal plane. The formula for the ideally imperfect crystal makes the intensity of reflexion to be proportional to  $q^2$ . It is our object in this paper to discuss which type of formula should be applied to actual crystals\*.

Many facts show that crystals must be regarded as imperfect in the sense discussed here. (a) It was first shown by Darwin that the strength of reflexion by a crystal of rock-salt was far greater than could be accounted for by the formula (3). According to this formula, total reflexion in the first order should be included in a region 6'' in breadth

\* The most striking case of this nature is that of the diamond crystal, investigated by W. H. Bragg (Proc. Phys. Soc. Lond. vol. xxxiii. p. 304, 1921). A small diamond crystal was bathed in X-rays, and rotated through each position of reflexion. The planes give structure amplitudes of two types, one being  $\sqrt{2}$  times as great as the other for corresponding angles of incidence. The ordinates of the two curves, which pass through points representing intensities of reflexion for planes of each type, are also in the ratio  $\sqrt{2}$  to 1. If intensity were proportional to the square of amplitude they should be in the ratio 2 : 1.

(p. 680, D (II)) for a wave-length of  $1.11 \text{ \AA}$ . A total reflexion over this range only accounts for one-tenth of the efficiency of reflexion of white radiation observed by Moseley and Darwin (D (II), p. 684). It was concluded in D (II) for this reason that crystals must be imperfect, and it was shown that the formula for the ideally imperfect crystal gives a much more satisfactory estimate of the efficiency of reflexion. (b) The formula for reflexion by a perfect crystal does not contain the absorption coefficient of X-rays in the material. Experiment shows that the absorption coefficient plays a large part in influencing the efficiency\*. (c) A direct experimental test shows that most crystals reflect monochromatic X-rays over so wide a range of angles that they must be composed of a mosaic of fragments only approximately parallel. In certain cases, however, the imperfection is too small to be observed in this way (calcite, diamond)†. In the case of calcite, as we shall see, other tests reveal the fact that it is not a perfect crystal for which the reflexion is given by formula (3).

#### 4. PRIMARY AND SECONDARY EXTINCTION.

It appears to us that the most promising method of discovering the physical nature of the crystal, and of deciding what formulæ to use, consists in careful measurements of the integrated reflexion. We may expect to find these measurements to lie between two extremes—a lower limit given by the formula for the perfect crystal, and an upper limit given by the formula for the ideally imperfect crystal. In order to estimate the degree of perfection we must have some idea of the behaviour of intermediate types, and this has been worked out in D (III). In this paper the ideally imperfect crystal is regarded as the standard, and the integrated reflexion is supposed to be lowered below this standard by two phenomena which are called primary and secondary extinction, which we may now explain. The formula for the perfect crystal shows that total reflexion takes place over a range of several seconds of arc in the case of the more powerful reflexions given by simple planes. In such a

\* W. H. Bragg, *Proc. Roy. Soc. A*, vol. lxxxix. p. 430 (1914).

† A very interesting note on imperfection of crystals has been published by H. Mark while this paper was being prepared (*Naturwissenschaften* 13, 49/50, p. 1042, Dec. 1925). By examining the divergence of the reflected X-ray beam from a diamond crystal at a distance of ten metres from the crystal, he has shown that some crystals of diamond are very nearly perfect.

crystal all the reflexion must take place in a layer very close to the surface, for the inner parts of the crystal receive no radiation at the correct angle for reflexion, since this radiation has been diverted by the upper layers. If, however, the crystal departs from ideal perfection, and the lower layers are inclined at an angle of more than a few seconds to the upper layer, they will be able to reflect radiation which has traversed the upper layers. *Any departure from perfection increases the integrated reflexion to a value greater than that given by formula (3).*

We have called this shielding of lower layers by parallel upper layers of the *same homogeneous fragment* of crystal "*primary extinction.*" It is at its maximum in the perfect crystal, and in fact it is not necessary to use the conception when dealing with the perfect crystal since formula (3) can be applied at once. It is convenient to use it when dealing with crystals which are imperfect, but in which the homogeneous blocks are so large that their lower layers are appreciably screened by the upper layers.

The upper limit to the integrated reflexion is given by formula (1) for the ideally imperfect crystal. In this case the homogeneous blocks are so small that every part of them receives its due of radiation. As long as the blocks are sufficiently small for this to be the case, their size and relative orientation do not affect the value of the integrated reflexion. This is only characteristic of the crystal, of the indices of the plane, and of the wave-length, when allowance is made for the effect described in the next paragraph.

A factor comes in which diminishes the integrated reflexion from that given by formula (1) even when the homogeneous blocks are very small. When the primary beam of X-rays traverses the crystal in a direction which permits of reflexion by some of the blocks, its energy is lessened by being partly reflected as well as by being absorbed in the usual way through conversion into  $\beta$  rays\*. The existence

\* The absorption coefficient of an amorphous substance contains a term arising from the scattering, which is quite small for moderately soft rays. If not insignificant, this term requires special treatment, as the scattering is responsible for the reflected wave. If the atoms had no heat motions, it would be proper to miss this part of  $\mu$  out, as its effect is allowed for in the secondary extinction below. At actual temperatures there is some general incoherent scattering, and this should be counted in with the true absorption; but the whole matter is involved in the question of the temperature effect, and requires much more thorough treatment. See Waller, "Theoretische Studien zur Interferenz und Dispersionstheorie der Röntgenstrahlen," Uppsala Universitets Årsskrift, 1925.

of this apparent increase in absorption at the reflecting angle was first demonstrated experimentally by W. H. Bragg\*. We have called this increase *secondary extinction*. In the case of a given crystal, its value will depend on the law according to which the fragments of homogeneous crystal are orientated, and on the direction in which the rays pass through the crystal. We have shown (BJB II) that in the case of the (200) reflexion from rock-salt the secondary extinction may attain a value half as great as the ordinary absorption coefficient, and very probably in other crystals it attains a much higher value.

Both primary and secondary extinction thus depend on the shielding of lower layers by parallel upper layers which divert X-ray energy which would otherwise be reflected. They may be distinguished as follows. In the case of primary extinction the upper and lower layers form part of the same homogeneous fragment of crystal, so that a phase-relationship exists between waves reflected by them. In the case of secondary extinction the layers are separated by other fragments with a different orientation, so that no such phase-relationship exists. In the first case the calculation deals with amplitude, in the second with intensity.

Both types of extinction tend to diminish the integrated reflexion to a value less than that given by formula (1), which therefore gives an upper limit to the intensity of reflexion.

In comparing the observed values of integrated reflexions with those given by formulæ (1) and (3), we are confronted by the difficulty of estimating the factor denoted by  $F(2\theta, \lambda)$  and the temperature factor. The chief object of our experiments on intensity must be to evaluate  $F$ , and thereby the arrangement of the electrons in the atom; but, for our present purpose, as we are only working out the order of the effect to be expected by using the two formulæ for reflexion, we will assume values of  $F$  which are known from other evidence to be approximately correct. When  $\theta$  is small,  $F(2\theta, \lambda)$  is equal to  $A$ , where  $A$  is the number of electrons in the atoms†, which are supposed to be identical

\* W. H. Bragg, *Phil. Mag.* vol. xxvii. p. 881 (1914).

† This assumes that the X-ray frequency is higher than any natural frequency in the atom. For heavy atoms it will be necessary to make an allowance for approximate equality of frequencies. Such a correction can be calculated by the ordinary principles of the theory of optical dispersion. Mark and Szilard (*Zeit. f. Phys.* xxxiii. p. 688, 1925) have obtained direct evidence of an abrupt change in the scattering power of an atom when the frequency of the incident radiation passes through the value characteristic of the absorption edge of the atom.

and arranged in a simple space-lattice (the extension to more complex cases involving several kinds of atoms is obvious). As  $\theta$  increases,  $F(2\theta, \lambda)$  falls away from this value in a way determined by the atomic structure. The values for  $F$  must be estimated by postulating probable atomic structures, and so are uncertain\*. They are probably not far from the truth, however, for low values of  $\theta$ , since the limiting value for  $\theta=0$  is definite.

In connexion with the theoretical value for  $F$ , the question arises whether an allowance should be made on account of the Compton effect, the change in frequency of part of the scattered radiation. It is conceivable that the change in frequency will prevent interference; and since part of the scattered radiation is thus changed, an estimate of the scattering power of the atom based on the classical theory and the laws of interference will be too large. This point needs, however, very careful theoretical investigation. From another point of view, if we make use of the close analogy between the Compton scattering and the Doppler effect, the Correspondence Principle suggests that the effect might have little influence in reducing the reflexion.

However this may be, it is evident that the doubt attaching to  $F$  applies mainly to large values of  $\theta$ , since the limiting value for  $\theta=0$  is definite. In the region of small glancing angles ( $\sin \theta < 0.1$  for Rh  $K\alpha$  rays, for example) the value of  $F$  has not fallen greatly from its maximum, and is almost independent of the exact assumptions made as to electronic configuration. In the same region the temperature factor is nearly unity. Extinction plays its most important part for the strong reflexions at small angles, since it is greatest when the integrated reflexion is greatest. *We may therefore hope to estimate the effect of extinction, and get some information about the mosaic structure of the crystal, by comparing calculated and observed intensities of reflexion at small angles where the uncertainty about the other factors at least.*

\* Hartree (Phil. Mag. vol. 1. p. 289, 1925) has calculated tables from which  $F$  curves for all atoms can be deduced. The classical law of scattering by an electron is assumed. The atomic fields for some atoms have been found approximately by numerical analysis of the optical and X-ray spectra, and thus the dimensions of each electronic orbit have been calculated, together with the timespent in every part of it. It is possible to generalize the results and put them in such a form that an approximate  $F$  curve for any atom can be constructed very simply. The modified distribution of quantum numbers due to Stoner is assumed, but the difference between  $F$  curves calculated with Stoner's or with Bohr's assumptions is quite small.

## 6. COMPARISON OF THE ESTIMATES OF INTENSITY GIVEN BY THE FORMULÆ WITH OBSERVED DETERMINATIONS.

(a) *Rock-salt*.—We give in the first place the figures for this crystal because we have investigated it more fully than others. Sufficient experiments have been carried out to enable an estimate of the temperature factor and of the effect of secondary extinction to be made. The effect of temperature on intensity has been measured by one of the authors\* between  $300^{\circ}$  and  $800^{\circ}$  absolute, and the measurements have recently extended to  $100^{\circ}$  absolute. Though the experiments at low temperatures are not yet completed, we may estimate the temperature factor at room temperature to be

$$e^{-6.44 \sin^2 \theta},$$

this being the reciprocal of the factor required to reduce measurements of intensity to absolute zero. In calculating this factor it is safe to assume that formula (1) is true for rock-salt in the higher orders of reflexion, since the effect of both kinds of extinction proves to be very small for weak reflexions. The extinction factors measured by us (BJB II) are, of course, characteristic of the specimens of rock-salt we used, and will not apply to other cases. As has been shown in D(III), the method we employed for determining them gives correct results for secondary extinction, but does not determine primary extinction.

The results of the comparison will be seen from Table I. The first column gives the sine of the glancing angle, the second gives  $F \dagger$ . The third and fourth columns give the integrated reflexion calculated by formulæ (3) (perfect crystal) and (1) (ideally imperfect crystal). Columns 5 and 6 show the effect of applying the correction for extinction, and for the temperature factor, the fourth column. In column 7 both corrections have been applied. Column 8 gives the experimental results.

The very great difference between the results of the two formulæ in columns 3 and 4 at low angles will be noticed, the one being one-fiftieth of the other. Extinction makes a large difference to the strong reflexions, but its effect is inappreciable for the high orders. On the other hand, the temperature factor which is nearly unity at low angles has a marked importance in the high orders, reducing reflexions to one-tenth their intensity when  $\sin \theta = 0.6$ . The figures

\* R. W. James, *Phil. Mag.* vol. xlix. p. 585 (1925).

† The  $F$  referred to is  $F_{\text{Ci}} + F_{\text{Na}}$ , and the reflexions are all from planes where the contributions from these atoms are in phase.

in the last two columns give a comparison between observed values and those to be expected from an ideally imperfect crystal. They prove that rock-salt must realize closely the true mosaic type.

Rock-salt, NaCl. Rh  $K_{\alpha}$  rays,  $\lambda = 0.614 \text{ \AA}$ .  $\mu = 10.7$ .

Sin $\theta$ .	F ( $F_0 = 28$ ).	$\rho \times 10^6$ , calculated for perfect crystal.	$\rho \times 10^6$ , calculated for ideally imperfect crystal.				$\rho \times 10^6$ , observed.
			No corrections applied.	Corrected for extinction.	Corrected for tempe- rature.	Both corrections applied.	
0.05	26.7	53.98	3004				
0.1	23.2	23.40	1148	725	1076	678	605
0.2	16.7	8.29	284.5	251	220.3	194.5	138
0.3	14.2	4.57	127.5	123.5	71.4	69.2	37
0.4	11.2	2.60	55.5	55.0	19.2	19.1	8.7
0.5	8.3	1.45	21.5	21.5	4.28	4.28	1.5
0.6	6.4	0.86	10.0	10.0	0.98	0.98	

The observed figures are all lower than the calculated figures. If the difference were due to primary extinction arising from high perfection of the crystal, one would expect the difference to be most marked at low angles. The reverse is the case, and it is more reasonable to suppose that the discrepancies are due to errors in the calculation of F. We have used the values given in Hartree's paper \*, calculated from his models of the electronic orbits in atoms. There is a general indication in all our results that Hartree's values do not fall away sufficiently fast as  $\theta$  is increased.

In a strict comparison we should allow for the temperature factor in giving the figures for a perfect crystal, and also calculate the effect of ordinary absorption. This is inappreciable for strong reflexions, but even in a perfect crystal it has an effect for the very weak reflexions. The figures at the bottom of column 3 will be considerably reduced by these corrections. When the amount of energy lost by absorption at a single crystal plane becomes appreciable as compared with that reflected, the formula becomes very complicated. Since the criterion for perfection becomes the more exacting the weaker the reflexion, and we have

\* *Loc. cit.*



already good evidence for imperfection in the strong reflexions, it seems unnecessary to evaluate the correct figures at the bottom of the third column. As indicated in D (II), the formula involves elliptic integrals.

(b) *Fluorspar*,  $\text{CaF}_2$ .—Reflexions for which the calcium and fluorine atoms are in phase have been measured for values of  $\sin \theta$  between 0.2 and 0.77. In this case the secondary extinction and temperature factor have not been measured, and the corresponding corrections to the figures calculated for the imperfect crystal cannot be made.

Fluorspar,  $\text{CaF}_2$ . MoK $\alpha$  rays,  $\lambda = 0.710 \text{ \AA}$ .  $\mu = 31.3$ .

Sin $\theta$ .	F ( $F_0 = 38$ ).	$\rho \times 10^6$ , calculated. Perfect crystal.	$\rho \times 10^6$ , calculated. Ideally imperfect crystal.	$\rho \times 10^6$ , observed.
0.05	36.3	107.8	3622	
0.1	32.4	48.0	1303	
0.2	21.6	15.7	304	112
0.3	14.0	6.6	79.0	47.0
0.4	11.2	3.8	39.6	18.2
0.5	9.9	2.55	19.5	9.0
0.6	8.1	1.60	10.2	4.8
0.7	6.0	0.91	5.0	2.6

The F values for calcium are taken from Hartree's tables. The F curve for fluorine taken from Hartree's tables has been modified, because in this crystal a comparison of the curves for  $\text{Ca} + \text{F}_2$ ,  $\text{Ca}$ , and  $\text{Ca} - \text{F}_2$  enables one to deduce that the F values for fluorine fall away more rapidly. F becomes less than 0.5 when  $\sin \theta > 0.55$ . We have similarly modified his values for oxygen in the following comparisons.

The temperature factor and extinction factor will reduce the figures in column 4 so that it again appears that fluorspar is of the imperfect mosaic, rather than of the perfect crystal, type.

(c) *Barytes*  $\text{BaSO}_4$ .—The structure of barytes, analysed by James and Wood\*, is more complex than that of the two crystals previously considered, and it is no longer possible to make measurements of reflexions for which all the atoms of the lattice unit are in phase. Since the barium, sulphur, and two of the oxygen atoms lie on symmetry planes

\* James & Wood, Proc. Roy. Soc. A, vol. cix. p. 588 (1925).

of reflexion in the crystal, and the only atoms not on these planes are the remaining two oxygen atoms of the molecule, which are very light in comparison, reflexions from these planes are nearly as strong as they would be if all the atoms had been in phase. The strength of these reflexions shows that the crystal approaches the ideally imperfect type. It is therefore justifiable to assume that  $\rho$  varies as the square of the structure amplitude, and to use this relation to construct a normal curve of intensity of reflexion from the observed results. The points on the normal curve are estimates of what the intensity would be if all the atoms had co-operated. The figures for this normal curve are given in the last column as "observed." In many cases the correction to be applied to the intensities for structure factor is not large, so that the normal curve so constructed cannot be far from the truth.

The absorption coefficient  $\mu$  for barytes has not been directly measured. The figure 116 for Mo  $K_\alpha$  radiation is calculated from tables given by Windgarth\*. In the case of other crystals we have found good agreement between the values given by his tables and measurements made with sections of crystal. We have not as yet investigated the extinction factor and temperature factor. The absorption coefficient is so high that the figures for reflexion from a perfect crystal, in calculating which no account of absorption has been made, are meaningless at the higher angles.

Barytes, like fluorspar and rock-salt, appears to be a crystal approaching the ideal mosaic type.

Barytes,  $\text{BaSO}_4$ . Mo  $K_\alpha$  rays,  $\lambda = 0.710 \text{ \AA}$ .  $\mu = 116$ .

Sin $\theta$ .	F ( $F_0 = 104$ ).	$\rho \times 10^6$ , calculated. Perfect crystal.	$\rho \times 10^6$ , calculated. Ideally imperfect crystal.	$\rho \times 10^6$ , observed.
0.05	100	140.1	1611	
0.1	89.3	62.4	648.5	462
0.2	65.6	22.5	168	127
0.3	50.5	11.3	61.6	33.8
0.4	41.0	6.59	27.8	11.3
0.5	32.1	3.90	12.3	4.6
0.6	27.0	2.52	6.78	2.06
0.7	24.5	1.55	5.0	

\* *Zeitsch. f. Phys.* vol. viii. p. 363 (1922).

(d) *Calcite*,  $\text{CaCO}_3$ .—This case is interesting because calcite appears to approach more closely the perfect crystal. The intensities in the last column are taken from relative measurements by W. H. Bragg\*, supported by an absolute determination of a few reflexions†. W. H. Bragg notes the fact that intensity in calcite appears to be proportional to structure amplitude rather than to its square. Ewald comments on this in his paper referred to above‡.

Calcite.  $\text{CaCO}_3$ . Rh  $K_\alpha$ ,  $\lambda=0.614 \text{ \AA}$ .  $\mu=15.6$ .

Sin $\theta$ .	F ( $F_0=50$ ).	$\rho \times 10^6$ , calculated. Perfect crystal.	$\rho \times 10^6$ , calculated. Ideally imperfect crystal.	$\rho \times 10^6$ , observed.
0.1	41.2	30.9	1220	240§
0.2	25.6	9.4	280	70
0.3	15.9	3.8	63	27
0.4	12.2	2.08	23.5	8.6
0.5	10.4	1.69	12.5	2.4

The low values of the observed intensities indicate that primary and secondary extinction must be much more important than absorption in reducing the intensity of reflexion. This is in accord with the observed proportionality of intensity to structure amplitude. This very interesting feature indicates the desirability of a more searching investigation.

A crystal which has a high primary extinction for strong reflexions may at the same time behave as a mosaic crystal for weak reflexions. In the latter case the range of perfect reflexion is smaller, and a larger homogeneous block is required in order to give complete reflexion. If the strong

\* Phil. Trans. Roy. Soc. A, vol. ccxv. (1915).

† W. L. Bragg, Proc. Roy. Soc. A, vol. cv. p. 16 (1924).

‡ The first measurements of absolute intensity of reflexion by Calcite were made by Compton (Phys. Rev. x. p. 95, 1917), who found that the intensity had a very much smaller value than the mosaic theory would lead us to expect. Davis and Stempel (Phys. Rev. xvii. p. 608, 1921) found that over a small range of angles a calcite crystal acts as a very good reflector of X-rays, as much as 44 per cent. of the radiation being reflected in certain cases. This range of reflexion was confined to about eighteen seconds of arc for the radiation which they used.

§ This figure is an estimate based on the observed intensity 149 for the (200) reflexion.

reflexions show an agreement in order of magnitude between observation and calculation by the mosaic formula (1), one can be certain that the weak reflexions obey formula (1) rigidly. The intensities of these reflexions will give reliable information about the form of the  $F$  curves at higher angles, provided that the effect of temperature can be allowed for. A knowledge of the temperature coefficient for  $\text{NaCl}$ ,  $\text{CaF}_2$ ,  $\text{BaSO}_4$ , and other crystals will thus make possible the determination of a set of empirical  $F$  curves which should be very useful in crystal analysis.

## 7. THE ESTIMATION OF THE DEGREE OF IMPERFECTION.

The preceding examples show distinct evidence that some crystals are nearly if not quite ideally imperfect, while in others there is a partial approach to perfection. It thus becomes important to gauge the degree of perfection, and the numerical results suggest that it is natural to regard the ideally imperfect as the standard and to gauge the departure from this. The chief object is to find the form of  $F$ ; but in the course of the work we may hope to derive information as to the actual degree of imperfection of any crystal.

The main difficulty in finding  $F$  (or, rather, the associated function  $Q$ ) lies in the evaluation and elimination of the extinction, a process which has only so far been carried out in the case of  $\text{NaCl}$ . We have pointed out above that there are two types of extinction simultaneously operative and that no process can eliminate one, the primary. The reason for this is that the primary extinction depends on the individual fragments, of which each reflects the rays over a few seconds of arc. If it were possible to obtain readings with the crystal at successive settings at intervals only a fraction of a second apart (the rays must be parallel with this degree of accuracy also), we might fit the results to a formula, find the number of layers in the fragments, and extrapolate to the case of small thickness. But the difficulty of doing this is very great, and we have to be content with the integrated reflexion of the fragments. The result of this is that we do not determine  $Q$ , but a lesser quantity  $Q'$ . It is shown in D (III), p. 816, that

$$Q' = Q (\tanh mq/mq), \quad . \quad . \quad . \quad (4)$$

where  $q$  is the amplitude of the wave reflected from a single plane, and  $m$  is the number of planes\*.

\* We owe to a letter from L. Waller the information that this formula only holds for reflexion at a face. For reflexion through a plate it is somewhat modified.

The matter is quite otherwise for the secondary extinction. This depends on the impoverishment of the radiation striking the deeper fragments on account of the reflexion from the outer ones. In this case it is possible to measure not merely the integrated reflexion, but the actual amount  $E_u$  at each setting  $u$  of the crystal (compare the curve in BJB II, p. 13). It was suggested in D III that from this curve it should be possible to deduce a function of the setting angle  $u$ , called  $G(u)$  (pp. 811 and 921), from which  $Q$  could be determined by integration over all values of  $u$ . The quantity  $G(u)du/Q'$  is the fraction of the crystal by volume in which the fragments are orientated with settings between  $u$  and  $u+du$ . Again, knowing the form of  $G(u)$ , it should be possible to calculate the extinction coefficient  $\epsilon$ , this being the addition to be made to the ordinary absorption coefficient in (1) so as to be able to derive  $Q$  from the integrated reflexion.

This quantity was directly measured in BJB II by taking the integrated reflexions *through* a set of crystals of varying thickness, instead of making the observations on a single crystal face. When a crystal plate of thickness  $t_0$  is rotated, and the rays are reflected at planes which are at right angles to the plate, the integrated reflexion is given by

$$\rho = Qte^{-\mu t},$$

where  $t = t_0 \sec \theta$ , and  $\mu = \mu_0 + \epsilon$ . By plotting  $\rho$  against  $t$  both  $Q$  and  $\mu$  can be measured. The ordinary coefficient of absorption  $\mu_0$  ( $10.7$  for Rh  $K_\alpha$ ) is measured by passing the rays through the plate at an angle where reflexion does not occur, and so  $\epsilon$  can be obtained. A value of  $5.6$  for  $\epsilon$  when the (200) reflexion is taking place, and of  $2.9$  for (220), was observed, these values being average ones for the specimens of rock-salt employed.

A calculation in D III made with the object of comparing these values of  $\epsilon$  with values based on the  $G(u)$  curve gave distinctly unsatisfactory results—the calculated value of  $\epsilon$  was about 1 as compared with the observed of about 5, though the data were perhaps not good enough to condemn the process out of hand. The matter has since been investigated with great skill and accuracy by Wasastjerna\*, who obtained much the same results, and there was thus a rather serious discrepancy to be faced. It would appear that this

\* By an ingenious slit-system, Wasastjerna explored the amount of radiation reflected at different depths of a crystal face. His value for  $\epsilon$  is close to that given in BJB II.

discrepancy is due to a fact overlooked in D III. The assumption was made that the crystal was uniform in character throughout, so that all points of its face possess the same  $G(u)$ . But if the gross structure of the crystal is warped, it is possible that the part illuminated through the top of the slit will reflect best in a different position from that illuminated through the bottom. All parts of the crystal may contribute to measurements of the stationary reflexion  $E_u$ , and so the reflexion curve may be spread out quite wide; but yet the crystal fragments in each part of the face may be strongly concentrated in one direction, with consequent large extinction. In fact  $G(u)$  must be regarded as a function of  $y$ , the coordinate along the axis of rotation, and  $E_u$  as a rather complicated average effect from which the corresponding average for  $G(u)$  cannot be derived. The function  $G(u)$  which comes into our formula depends on the divergence in orientation from a mean direction of the fragments encountered along the path of a reflected beam, which will be only a fraction of a millimetre in length within the crystal. It depends on the local imperfection, not the gross imperfection, of the crystal.

We may observe that this difficulty does not arise in the experimental method of BJB II, for there only averaged quantities occur throughout; but it is necessary to assume that the warping was about the same in extent for all plates used.

The other problem is to measure the mean of the depth of the coherent fragments. If  $Q$  is known from other sources, we can deduce this by measuring  $Q'$  and so solving (4) for  $mq$ , for  $q$  is determined by  $Q$ . But if the problem is to determine  $Q$ , this method is not available. All we can do is to take various crystals of the same substance (of which some should preferably show external signs of being fragmented), and evaluate  $Q'$  for each of them. The greatest value may be presumed to be not far from  $Q$ .

The experimental data are insufficient to apply this method yet, but to illustrate it we shall suppose that in the rock-salt above the difference between the last two columns is due to primary extinction.

Then we have  $\frac{\tanh mq}{mq} = \frac{605}{678}$ ,  $mq=0.61$ , and since  $q=2 \times 10^{-4}$ , we have  $m=3050$  as the average number of planes in a fragment. As pointed out above, it is probable that the difference between 605 and 678 is due rather to an error in  $F$  than to extinction. If so, the fragments must be thinner than this.

To summarise :—We have three different types of imperfection—those responsible for primary and for secondary extinction, and the general warping of the crystal. Unless we know  $F$  from other sources, the first can only be evaluated by investigating so many crystals that in some the correction is absent. When known it tells us how thick the perfect fragments of each crystal specimen are. The second can be found by direct experiment, and tells us the angular width over which the fragments are spread in each part of the crystal. The third is of the type usually to be seen directly by the surface reflexion of ordinary light. It could be studied by taking reflexion curves with varying lengths of the slits defining the beam of X-rays.

#### 8. THE EARLIER ARGUMENTS IN FAVOUR OF CRYSTAL IMPERFECTION.

The evidence for considering crystals as imperfect is quite conclusive, as shown in § 6 above ; but this conclusion was, in fact, reached in 1914 in D (I) and D (II). The argument as there given is not very clearly expressed, and is enormously complicated by the fact that no double reflexions had then been made, so that the only experimental measure of efficiency of reflexion had to do with white radiation. There were two stages in the argument. In D (I) it was shown that it was not possible to disregard the interactions between the atoms, and in D (II) that, allowing for the interactions as they would occur in a perfect crystal, the total amount reflected was far below the amount observed.

The first argument was as follows :—Supposing that the wave scattered by each atom is too small to influence the others, we can calculate the diffraction pattern of the reflected wave when a fixed crystal is illuminated by the spherical waves from a point-source. The pattern is like those in the lateral spectra of a grating, and the only limitation to the number of lines of the grating is the absorption coefficient of the crystal. A simple calculation shows that the number is enormous, and that the angular breadth of the image is only about  $1/100$  of a second of arc. We may notice that this in itself is sufficient for the purpose in view, for even if the reflexion in that breadth were perfect, it would make the integrated reflexion equal to about  $1/2,000,000$ , and we now know it to be often more than  $1/10,000$ . In D (I), however, a more cautious line of argument was taken, and one approximating more closely to the experiments. In the first place we assume the formulæ to be correct, and

apply them to the curves of white radiation as measured by Moseley and Darwin. The higher orders of spectra and the peaks of characteristic radiation are easily eliminated, and the result is a curve for  $E_\lambda$ , the distribution of energy in the spectrum (a table of the values is given in D (I), p. 331). Next consider the experimental measure of efficiency of reflexion. The incident waves were limited by a slit, so that their angular aperture was, say,  $\delta\theta$  broad. Thus a certain range of wave-lengths would be reflected, say  $\delta\lambda$ , which would be determined by the relation  $\lambda = 2a \sin \theta$ , so that  $\delta\lambda = \lambda \cot \theta \delta\theta$ . The radiation reflected would be proportional to  $\delta\lambda$ , and the incident radiation through the same slit to  $\delta\theta$ , so that the ratio of the two is independent of the slit's breadth. Now, we can certainly say that the amount of radiation reflected must be less than  $E_\lambda \delta\lambda$ , for this is the whole amount of radiation of reflectable wave-length that falls on the crystal. So we have as an upper limit to the reflexion an amount  $E_\lambda \lambda \cot \theta \delta\theta / \int_0^\infty E_\lambda d\lambda$ . In this all

quantities are definite except  $\delta\theta$ , and to get the best upper limit we want to know how small this may be taken. The value of  $\delta\theta$  was fixed in D I by the condition that it was to be the smallest value which would not markedly alter the conditions of the experiment. It was shown (p. 323) that with the actual experimental arrangements, if the slit was less than about  $5''$  broad, the intensity of the reflexion would suffer on account of diffraction, and so this was the value chosen. It would really have been possible to modify the argument so as to make  $\delta\theta$  far smaller, for, in fact, the incident radiation would have suffered in the same way as the reflected, but the argument would be complicated because each part of  $\int_0^\infty E_\lambda d\lambda$  would be affected to a different extent.

Thus the angle  $\delta\theta$  was chosen at  $5''$ , because this was the smallest value which would be admissible without markedly altering the experiment. It was quite sufficiently small, as it gave an upper limit about  $1/10$  of the actually observed radiation. It was this fact that showed that it was wrong to neglect the interactions of the atoms, and led to the investigations of D (II).

The second argument deals with the formulæ for a perfect crystal, and is much simpler. We have seen that the reflexion is perfect in a region of a few seconds of arc, and that this region is responsible for three-quarters of the whole reflexion.



It is necessary, of course, to carry over the calculation so as to deal with white radiation ; but this is quite straightforward, and the argument goes as before, but now with four-thirds of the angle of perfect reflexion taken as  $\delta\theta$ . Again, it was found that the reflexion was ten times as great as it should be.

Since in both cases the difficulty depended on the exceedingly narrow angle of the reflexion, it was obvious that it could only be met by increasing this angle, and that could only be done by supposing the crystal imperfect, so that there would be several reflexions.

#### MATHEMATICAL NOTE.

In D(III), p. 814, a rather complicated integral occurs in connexion with primary extinction, which happens to simplify in a remarkable way. The formal proof was not found until the paper was in the press, and so could only be given shortly in a footnote. It is not easy to follow, and we take this opportunity to give a more detailed proof.

Omitting certain factors which are mathematically irrelevant, the integral is

$$I = \int_{-\infty}^{\infty} \frac{du}{|iu + \sqrt{q^2 - u^2} \coth m \sqrt{q^2 - u^2}|^2}.$$

The second term in the denominator is single valued, and is real whether  $q$  or  $u$  is the greater. Hence we write the integral as

$$I = \int_C \frac{du}{2u} \left\{ \frac{1}{u - i \sqrt{q^2 - u^2} \coth m \sqrt{q^2 - u^2}} + \frac{1}{u + i \sqrt{q^2 - u^2} \coth m \sqrt{q^2 - u^2}} \right\},$$

where  $C$  is a contour following the real axis from  $-\infty$  to  $-\eta$ , then going over a semicircle above the real axis to  $\eta$ , and then following the real axis to  $\infty$ , and  $\eta$  is to tend to zero. Now, if we cut the real axis between  $\pm q$  and take  $\sqrt{q^2 - u^2}$  as positive when  $u$  is pure positive imaginary, it is not hard to show that the real part of  $\coth m \sqrt{q^2 - u^2}$  is always positive above the real axis and negative below. Also  $u/i \sqrt{q^2 - u^2}$  has its real part positive over the whole plane. Hence the first term in the integrand has no poles

below the real axis, and the second none above. We can thus deform the contour for the second term to infinity above the real axis, and it is easily seen to vanish over the finite arc. The first term can be similarly treated, but in this case it must first be taken across the origin. Thus the integral is altogether equivalent to the integral of the first term taken negatively round a small circle above the origin, and this gives

$$I = \pi \tanh mq/q,$$

which is the required result.

#### SUMMARY.

The present paper is a review of theoretical and experimental work on the intensity of reflexion of X-rays by crystals. In 1914 Darwin evaluated expressions for the relation between the amount of radiation reflected by a crystal face and the incident X-ray energy. The form of these expressions was shown to depend on the assumptions made as to the interaction between waves scattered in different parts of the crystal. One of these expressions may be applied to the case where a crystal is composed of a mosaic of small blocks, which are only approximately parallel to each other. Moseley and Darwin in 1913, and Compton in 1917, showed that the results of experimental comparisons of incident and reflected energy are of the right order to be accounted for by this formula. W. H. Bragg in 1914 developed an experimental technique for getting comparative measurements of the intensity of reflexion by different faces with the ionization spectrometer. He also first observed the effect of the temperature factor, and showed that extinction took place in the crystals when the rays traversing it were being reflected. His methods of measurement were used by Compton in 1917 and by the authors in 1921, being extended so that an absolute comparison of incident and reflected energy could be made. The other expression for intensity of reflexion evaluated in Darwin's 1914 paper applies to the case of a perfect crystal. Ewald in 1917 attacked the problem of the diffraction of radiation by a perfect crystal, and arrived independently at the same results. Reflexion from a crystal face is shown to be perfect over a small range of glancing angles, the extent of which is proportional to the efficiency with which each crystal plane reflects the radiation. In a series of papers (Bragg, James,

and Bosanquet, 1921) quantitative measurements were made on sodium chloride which supported the accuracy of the formula for the mosaic crystal, and led to a determination of the scattering powers of sodium and chlorine over a wide angular range.

These results were discussed in a paper by Darwin in 1923, and a more complete theory of reflexion by the imperfect crystal was developed. Recently (1925) Ewald has drawn attention to the fact that results obtained with some crystals (calcite, diamond) appear to support the type of formula which applies to a perfect crystal rather than that which applies to the imperfect mosaic. In particular, Ewald discusses a series of measurements on diamond made by W. H. Bragg.

In this paper we have discussed the evidence as to the nature of crystals. This question must be decided before quantitative analysis can be applied, and one may hope for two interesting results from successful analysis. In the first place, it would lead to a knowledge of the scattering power of the atoms, which would be the most direct evidence we have as to the distribution of electrons in the atom. In the second place, in analysing crystal structure we need to know both the scattering power of the atoms and the type of formula which applies to the reflexion. As Ewald has pointed out, the formula for the perfect crystal makes the intensity of reflexion proportional to the structure amplitude. The formula for the imperfect crystal, on the other hand, makes the intensity proportional to the square of the structure amplitude, and this is the relation generally assumed in analysis. We find that most crystals are of the imperfect rather than of the perfect type, but their perfection is sufficiently high to make it necessary to modify the mosaic formula. These modifications take the form of corrections for primary and secondary extinction in the crystal, examined by Darwin in 1923 and further discussed in the present paper. A series of examples are given in which the observed intensities may be compared with those obtained by the two formulæ for the perfect and for the mosaic crystal respectively.

LXXXII. *On Professor Joly's Theory of Earth History.*

By HAROLD JEFFREYS, M.A., D.Sc., F.R.S. \*

1. **I**N his book 'The Surface History of the Earth' and in several previous papers Prof. J. Joly has offered a far-reaching theory of the thermal history of the Earth and its geological consequences, based on the hypothesis that so much heat is generated in the interior by radioactivity as to lead to widespread fusion. Some of the fundamental data of his discussion, however, appear to be very questionable, and at several subsequent stages it is doubtful whether the consequences would be those inferred by Prof. Joly.

The initial assumption is that the thickness of the granitic layer of the continents is about 30 km.; three independent lines of argument seem to point to such a value. The whole of the subsequent development depends on this supposition, which therefore requires careful scrutiny. It must be pointed out that two of the estimates are really upper limits, while the other is an order of magnitude; none of them can be regarded as a measure.

The first estimate is obtained by finding the heights of granite and basalt columns that would give isostatic balance together with the observed difference in mean level between the continents and the oceans. There is, however, strong reason for believing that another material besides granite and basalt is involved. The velocity of compressional elastic waves in the upper crust is about 5.4 km./sec., agreeing with what we should expect from laboratory measures on granite under pressure. But all compressional waves that penetrate below the granite layer show a velocity of at least 7.2 km./sec. †, which is substantially greater than the velocity appropriate to basalt or diabase under the pressures involved, but agrees with experimental knowledge for peridotite; dunite gives 7.4 km./sec. ‡. There is no direct seismological evidence of the existence of basalt below the continents, and the basaltic layer may therefore be fairly thin; but the lower layer must consist of a denser and more rigid material extending to a depth of some hundreds of kilometres. It is natural to identify this with peridotite, of density 3.4, or with some still denser material. This

\* Communicated by the Author.

† Knott, from the Zöppritz-Turner tables, gives 7.18 km./sec.; other writers give 7.8-8.0 km./sec. Cf. B. Gutenberg, *Der Aufbau der Erde*, p. 97.

‡ E. D. Williamson and L. H. Adams, J. Frank. Inst. cxv. pp. 475-529 (1923).

material is at least as likely as basalt to constitute the suboceanic material that balances the continents, and if so the depth of the granitic layer need only be about 16 km.

The second estimate, due to Oldham, is based on the distance from the epicentre where the P and S phases of a seismic disturbance become distinct; but this involves numerous complicating factors, and can hardly be considered to give more than an order of magnitude. On the other hand, the velocities of Love waves indicate a thickness of about 15 km.\*

The third estimate is based on the fact that the radioactivity in 30 km. of granite in a steady thermal state would just supply the heat that is being conducted out of the Earth. But the apparent agreement would break down if some of the heat rising to the surface is due to the original heat of the Earth, and this may well be appreciable. Thus this estimate is an upper limit to the thickness of the granitic layer.

2. The basic rocks below the granitic layer also contain radioactive matter, and it is upon the heat generated in them that Prof. Joly relies for his main object, which is to explain periodic variation of temperature within the crust. Now there are many soluble problems involving the steady supply of heat to a conducting solid with an outer boundary at a constant temperature, but they all have a common property, namely, that the temperature distribution tends asymptotically to a steady state; there is no possibility of periodicity. The reason for this may be understood by considering the one-dimensional flow of heat in a finite depth of uniform material.

The differential equation satisfied by the temperature  $V$  is

$$\frac{\partial V}{\partial t} - h^2 \frac{\partial^2 V}{\partial x^2} = \frac{P}{c\rho}, \quad . . . . . (1)$$

where  $t$  is the time,  $h^2$  the thermometric conductivity,  $x$  the depth,  $P$  the rate of supply of heat per unit volume, regarded as a function of  $x$ ,  $c$  the specific heat, and  $\rho$  the density. The terminal conditions we may suppose to be that  $V=0$  at the ends  $x=0$  and  $x=l$ . Then (1) and the terminal conditions are satisfied if  $V=V_0$ , where

$$V_0 = - \int_0^x \int_0^{\xi_1} \frac{P(\xi_2)}{c\rho h^2} d\xi_1 d\xi_2 + \frac{x}{l} \int_0^l \int_0^{\xi_1} \frac{P(\xi_2)}{c\rho h^2} d\xi_1 d\xi_2. \quad (2)$$

We have also an initial condition that  $V$  differs from  $V_0$  by

\* Jeffreys, M. N. R. A. S. Geoph. Suppl. 1, pp. 282-292 (1925).

$V_1$ , say, when  $t=0$ ;  $V_1$  can be expressed in a sine series of the form

$$V_1 = \sum_{n=1}^{\infty} A_n \sin \frac{n\pi x}{l} \dots \dots \dots (3)$$

Then all the conditions are satisfied if

$$V = V_0 + \sum_{n=1}^{\infty} A_n \sin \frac{n\pi x}{l} e^{-k^2 n^2 \pi^2 t / l^2}, \dots \dots (4)$$

which tends continuously to  $V_0$  as the time increases. The time inevitably enters through negative exponential factors and not through trigonometrical ones.

Prof. Joly's theory introduces two complications designed to avoid this result, but it may be questioned whether they succeed. The first is to suppose that a layer below the crust becomes liquid. The probable course of events in this case may be inferred from an analogue, which is easier to visualize than the thermal problem. If a stretched string in a viscous liquid, with the ends fixed, is slightly displaced from the position of equilibrium, its equation of motion is

$$\lambda \frac{\partial^2 \eta}{\partial t^2} + k \frac{\partial \eta}{\partial t} - T \frac{\partial^2 \eta}{\partial x^2} = F, \dots \dots (5)$$

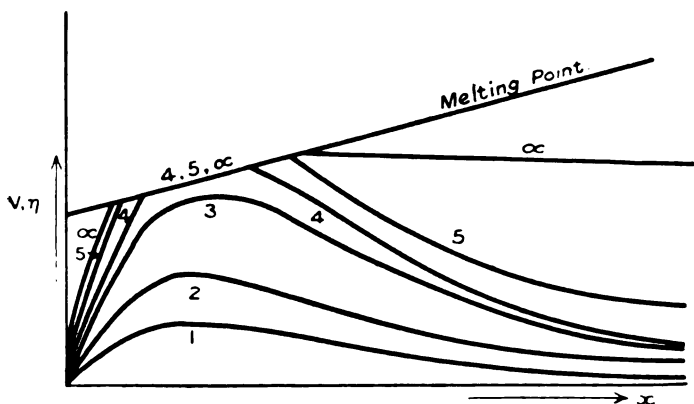
where  $\eta$  is the transverse displacement,  $\lambda$  the mass per unit length,  $k$  a constant depending on the viscosity,  $T$  the tension, and  $F$  the transverse force per unit length. If the motion is slow enough, or the viscosity high enough, the first term becomes negligible in comparison with the second, and the equation is indistinguishable from that for heat conduction. So long as the medium in the thermal problem is solid, therefore, there is a corresponding problem of a string, whose solution will give at once the complete solution of the thermal problem. The absence of periodicity from the motion of a string with very high damping is in accordance with ordinary experience.

When fusion occurs anywhere, the excess of the heat generated over that conducted away produces no further rise of temperature until the change of state there is complete. Afterwards convection will raise the new heat generated to the bottom of the still solid material, and thus fusion will gradually extend upwards. In the analogue of the string, the conditions of fusion will correspond to a fixed barrier; after an interval, corresponding to the time needed for the change of state, the force originally applied to the constrained region is transferred to its upper margin. The constrained region will extend until the gradient at the end is such that the transverse component of the tension there just

balances the whole of the applied force. No further change will occur.

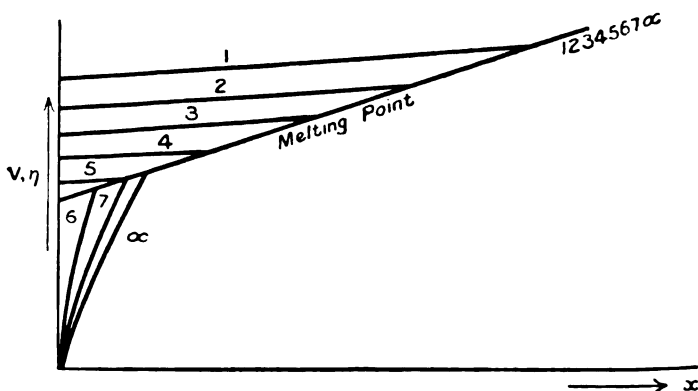
The above argument is qualitative, but appears plausible, and could be tested by experiment if desired. The course of the changes is given by the successive curves in fig. 1. The scale of  $\eta$  is, of course, much exaggerated.

Fig. 1.



Heating of an initially cold solid.

Fig. 2.



Cooling of a substance initially fluid. Curves show successive states; those marked  $\infty$  denote the ultimate steady states. The figures are believed to be qualitatively correct, but are not the result of calculation.

If the material is originally fluid, but is denser when solid than when fluid, the corresponding curves are as in fig. 2. In neither case does there seem to be any reason for assuming periodicity in the solution.

3. In the case of the Earth several cases may arise. Permanent solidification may occur everywhere, which is the view that I believe and have developed elsewhere; fusion may occur below the continents and not below the oceans; or fusion may occur below both continents and oceans. Prof. Joly adopts the last alternative, but not for any obvious reason. Even if we accept his view that continental conditions imply fusion temperatures at depths of the order of 30 km., there is every reason to suppose that the basic rocks of the ocean floor are much less radioactive, so that fusion may well fail to occur below the oceans. In that case the only effect of fusion below the continents would be to lift the continents up; there is no opportunity for movement into, or out of, the continental regions, and mere vertical expansion in fusion would not disturb isostasy.

Prof. Joly, however, assumes that at intervals the whole subcrustal region, below continents and oceans alike, becomes fluid, but that the surface rocks remain permanently solid. Tidal friction is then supposed to tow the crust around over the fluid layer, and the crust below the oceans is supposed to be much thinner than that below the continents. In these conditions rapid heat conduction through the sub-oceanic crust is supposed to restore solidity. It must be pointed out, however, that the melting points of rocks increase with the basicity; so oceanic rocks must, on the whole, have higher melting points than continental ones. If the crust below the oceans is thinner than that below the continents, it follows, on both grounds, that the rate of outflow of heat through the ocean floor in the equilibrium state is much greater than that below the continents. Thus a greater supply of heat is needed below the oceans; whereas every previous consideration points to the greater supply of heat by radioactivity taking place below the continents.

This contradiction appears to arise from the statements on pp. 102-3 of Prof. Joly's book. "If (the substratum) is solid, the radioactive heat continually being developed . . . beneath the continents is almost entirely accumulated." "The blanketing effects of continental radioactivity . . . effectively block its escape by conductivity." It seems to be supposed that heating a region prevents the transmission of heat through that region; which is not the case. The equation of heat conduction being linear, the effects of all sources of heat are purely additive; radioactivity within the granitic layer can do absolutely nothing to prevent the transmission to the surface of the heat developed below, and only ensures that the temperatures below that layer become higher than they would in its absence.



Prof. Joly then supposes that solidity is restored everywhere by conduction through the ocean floor. But it seems that even if the crustal thickness varies in the way postulated by Prof. Joly, the only effect of the revolution of the crust would be to make the temperature distribution oscillate about a mean, this mean being nearly what would result if radioactivity at every depth were a mean of the values appropriate to land and sea conditions, weighted according to the area involved. If fusion in the steady state was involved below both land and sea, there seems no reason to believe that alternation between land and sea conditions will restore solidity ; it seems much more likely, in view of the above considerations, that after any transition the temperature distribution would tend asymptotically towards the equilibrium conditions in the new circumstances ; the depth of fluid everywhere would then always be between the values appropriate to continental and oceanic conditions.

4. There is a further difficulty in making the crust revolve at the required rate. Tidal friction is appealed to for this purpose ; but it is well known that perfect fluidity on an extensive scale in a crustal region is likely to abolish the ocean tides altogether. A thin crust of any reasonable rigidity is so flexible that it opposes an insignificant resistance to tidal deformation of a fluid layer more than a few kilometres deep below it\*, and its outer boundary therefore remains almost an equipotential surface throughout the tidal motion. There is therefore no force tending to move the ocean along the boundary, and there can be no ocean tides. The magma layer being itself a perfect fluid, there can be no dissipation of energy within it, and there is therefore no tidal friction.

Passing to the case of infinite viscosity in the intermediate layer (that is, perfect elasticity) we may have tidal friction in the ocean, but it cannot produce any permanent displacement of the crust. Permanent deformation of the crust, in fact, requires a rather delicate adjustment of conditions. Intermediate viscosities will give oceanic tides, and the tides in the magma layer will also lag ; both effects will give tidal friction, the latter being capable of giving the greater values on account of the higher density of the matter involved.

Let us then investigate the tides in a thin viscous fluid layer just below the surface. The outer crust is supposed thin enough to offer negligible opposition to the motion of the fluid, so that the upper boundary of the fluid will be

\* Love, *Proc. Roy. Soc.* (1908).

treated as free. The long wave approximation, that the variations of pressure are independent of the depth, will hold; also the depth considered by Prof. Joly, 100 km., is great compared with that which gives inversion of phase in the tides, so that the acceleration terms also will be negligible. The motion may then be treated as approximately laminar, and the equations of motion reduce to

$$\nu \frac{\partial^2}{\partial z^2} (u, v) = \frac{g}{a} \left( \frac{\partial}{\partial \theta}, \frac{\partial}{\sin \theta \partial \phi} \right) (\zeta - \bar{\zeta}) \quad (1)$$

in Lamb's notation. If  $h$  be the depth, the horizontal velocities must be proportional to  $2hz - z^2$ , where  $z$  is measured upwards from the bottom of the layer; whence

$$(u, v) = -\frac{g}{2\nu a} (2hz - z^2) \left( \frac{\partial}{\partial \theta}, \frac{\partial}{\sin \theta \partial \phi} \right) (\zeta - \bar{\zeta}) \quad (2)$$

The equation of continuity is

$$\frac{\partial \zeta}{\partial t} = -\frac{1}{a \sin \theta} \int_0^h \left[ \frac{\partial (u \sin \theta)}{\partial \theta} + \frac{\partial v}{\partial \phi} \right] dz, \quad (3)$$

$$= \frac{gh^3}{3\nu a^2 \sin \theta} \left[ \frac{\partial}{\partial \theta} \left\{ \sin \theta \frac{\partial}{\partial \theta} (\zeta - \bar{\zeta}) \right\} + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \phi^2} (\zeta - \bar{\zeta}) \right] \quad (4)$$

Now  $\zeta$  and  $\bar{\zeta}$  are surface harmonics, of order  $n$  say, so that

$$\begin{aligned} \frac{\partial}{\partial \theta} \left\{ \sin \theta \frac{\partial}{\partial \theta} (\zeta - \bar{\zeta}) \right\} + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \phi^2} (\zeta - \bar{\zeta}) \\ = -n(n+1) \sin (\zeta - \bar{\zeta}) \end{aligned} \quad (5)$$

Hence

$$\frac{\partial \zeta}{\partial t} = -\frac{gh^3}{3\nu a^2} n(n+1) (\zeta - \bar{\zeta}) \quad (6)$$

But  $\bar{\zeta}$ , the height of the equilibrium tide, is affected by the mutual attraction of the fluid. If the part due to the moon is  $\zeta_0$ , we have

$$\bar{\zeta} = \zeta_0 + \frac{3}{2n+1} \frac{\rho}{\rho_0} \zeta, \quad (7)$$

$\rho$  and  $\rho_0$  being the surface-density and the mean density of the Earth. Then

$$\frac{\partial \zeta}{\partial t} = -\frac{gh^3}{3\nu a^2} n(n+1) \left[ \zeta \left( 1 - \frac{3}{2n+1} \frac{\rho}{\rho_0} \right) - \zeta_0 \right], \quad (8)$$

and if the time factor is  $e^{\gamma t}$

$$\frac{\zeta}{\zeta_0} = \frac{n(n+1)gh^3/3\nu a^2}{\gamma + n(n+1) \left( 1 - \frac{3}{2n+1} \frac{\rho}{\rho_0} \right) \frac{gh^3}{3\nu a^2}} \quad (9)$$

Tidal friction is a maximum if the phase lag is  $\frac{1}{4}\pi$ , when

$$n(n+1) \left(1 - \frac{3}{2n+1} \frac{\rho}{\rho_0}\right) \frac{gh^3}{3\nu\alpha^2} = \gamma. \quad (10)$$

In the case of the semidiurnal tide  $n=2$ ,  $g=981$  cm./sec.<sup>2</sup>,  
 $1 - \frac{3}{2n+1} \frac{\rho}{\rho_0} = 0.6$ ,  $a = 6.37 \times 10^8$  cm.,  $\gamma = 14 \times 10^{-5}$ /sec.  
 Prof. Joly takes  $h=10^7$  cm. Then

$$\nu = 2.2 \times 10^{10} \text{ cm.}^2/\text{sec.}$$

gives the maximum frictional couple. The ratio of the amplitudes of  $\zeta$  and  $\zeta_0$  is  $\left(1 - \frac{3}{2n+1} \frac{\rho}{\rho_0}\right)^{-1} 2^{-\frac{1}{2}} = 1.2$ .

The frictional couple is \*

$$N = \frac{32\pi}{15} ga^2 \rho \lambda q^2 \sin 2\epsilon, \quad (11)$$

where  $g$  is the maximum amplitude of  $\zeta_0$ ,  $\lambda q$  that of  $\zeta$ , and  $2\epsilon$  the phase difference. Now if the outer shell is rotated over the interior with relative angular velocity  $\omega$ , the relative velocity at the top and bottom of the fluid layer is  $a\omega \sin \theta$ , and the rate of shear  $a\omega \sin \theta/h$ . The shearing force is therefore  $\nu \rho a \omega \sin \theta/h$ , and the couple required is

$$\begin{aligned} N &= \int \int \frac{\nu \rho a \omega}{h} \sin \theta \cdot a \sin \theta \cdot a^2 \sin \theta \, d\theta \, d\phi \\ &= \frac{8}{3} \pi \frac{\nu \rho a^4}{h} \omega. \end{aligned} \quad (12)$$

From (11)

$$N = 4 \times 10^{24} \text{ gm. cm.}^2/\text{sec.}^2,$$

approximately; so that

$$N/C = 5 \times 10^{-21}/\text{sec.}^2,$$

where  $C$  is the Earth's moment of inertia. The present value is about  $2 \times 10^{-22}/\text{sec.}^2$ . Also

$$\omega = 6 \times 10^{-16}/\text{sec.}$$

Thus it would take  $1.6 \times 10^{15}$  secs., or  $5 \times 10^7$  years, to displace an equatorial continent relative to the interior by 6000 km. This estimate of the time requires a further increase for three reasons. The yielding of the solid interior

\* Cf. Jeffreys, 'The Earth,' 14.21 (6) and (10).

will reduce the tides in the fluid layer, thereby at least halving  $\omega$ ; in the above discussion the upper surface has been supposed free, so that the velocities are overestimated; and the whole couple has been supposed applied to the enclosing shell, whereas actually it would be distributed through the fluid, giving a correspondingly slower displacement. Prof. Joly requires such a displacement to occur in  $3 \times 10^6$  years, and for this purpose, on his own numerical assumptions, tidal friction is inadequate.

Reducing the viscosity below  $2 \times 10^{10}$  cm.<sup>2</sup>/sec. will reduce the tidal friction, but the rate of crustal displacement will not be greatly affected, since it depends on  $(\sin 2\epsilon)/\nu$ , which remains finite when  $\nu$  tends to zero.

The discordance could be reduced by reducing the assumed value of  $h$ ; for the optimum value of  $\lambda$  is proportional to  $h^3$  and the associated  $\omega$  to  $h/\nu$  or  $h^{-2}$ . Reducing  $h$  to 20 km. would make it just possible to make this part of the theory self-consistent; but it is still necessary for viscosity throughout the displacement not to exceed considerably the value necessary to give the maximum tidal friction. Further, with a fluid layer of such a depth it is possible that the deeper projections on the under side of the outer layer would touch the bottom of the fluid layer and prevent all motion; and the reduction of the depth of the fluid would much reduce, and perhaps annihilate, the volume changes available for geological purposes.

5. To sum up, Prof. Joly's theory requires:—

(a) That the granitic layer of the continents should be about 30 km. thick, leading to fusion below it on account of excess radioactivity;

(b) That if fusion occurs, the upper solid layer should be much thinner below the oceans than in the continents;

(c) That tidal friction in such conditions should make the outer shell rotate with respect to the interior;

(d) That the result of such rotation should be to restore solidity in the liquefied layer.

If any one of these assertions is incorrect, the theory will fail. Reasons are given here for believing that all are incorrect. The estimate in (a) is probably excessive; the arguments for (b) are erroneous; with Prof. Joly's conditions tidal friction is not adequate for the purpose of (c); and, contrary to (d), fusion once initiated seems likely to be permanent.

LXXXIII. *The Surface History of the Earth.*

By J. JOLY, F.R.S.\*

**I**N his criticism of my theory of the surface history of the earth, Dr. Jeffreys commences with the statement that "the initial assumption is that the thickness of the granitic layer of the continents is about 30 km. . . . The whole of the subsequent development depends on this supposition. . . ."

Dr. Jeffreys's deduction is entirely mistaken. If the assumption of 30 km. is seriously wrong, one or other of two cases must arise. Radioactive heat derived from the upper part of the substratum would share in maintaining the surface gradient, or radioactive heat derived from continental rocks would flow downwards into the substratum. It is not improbable that the first condition arises in the case of so shallow a continent as Europe. The second case, as I have elsewhere pointed out (*Phil. Mag.* July 1923), probably arises in the case of parts of S. Asia. The very unequal thickness of the continents is pointed out in 'The Surface History of the Earth,' p. 53.

In this matter there is obviously latitude in the choice of data. In earlier estimates I arrived at 24 km. (*Phil. Mag.* June 1923). I think I have more than once pointed out that the principal teaching of such estimates is that the substratum beneath the continents must be near its melting-point, and that but little heat can be escaping from it, the major part of that which arises out of the surface gradient being ascribable to the continental rocks themselves.

Dr. Jeffreys, having concluded that a thinner continental crust than 30 km. must be fatal to the radioactive theory of surface history, then proceeds to show from certain seismic data that this crust must be about 15 km. thick. As I have said, the point is not of serious importance. However, it is of interest to note that so careful a writer as Dr. A. Holmes draws a different conclusion out of his examination of the available data, and adds: "Jeffreys concludes that the thickness of the granite shell is between 10 km. and 30 km., and favours an estimate of 15 km. This I believe to be an under-estimate, even on his own data. I would prefer to adopt limits of 25 and 30 km. as more probable, particularly as the important work of

\* Communicated by the Author.

Mohorovičić lends support to estimates even higher than 30 km.”\*

On the basis of the mean continental elevation over sea-level and the mean depth of the ocean, and assuming that the continents are granitic and float isostically in a basaltic substratum the surface of which is the ocean-floor, we arrive at a mean continental depth of 30·7 km. This is, I believe, the most direct estimate we possess. (Surf. Hist. of the Earth, p. 35.)

Dr. Jeffreys then argues for the existence of a peridotite layer beneath the continents, with a possible thin layer of basalt intervening. He considers that this would harmonize with the velocity of compressive seismic waves which penetrate below the continents. He states that all such waves penetrating below the granitic layer show a velocity of at least 7·2 km. per sec. Now, there is much that is precarious about seismic evidence, and in this case there are quite contrary deductions available. Thus, Mohorovičić (*Beit. zu Geophysik*, 1913 & 1914) gives the average velocity of compressional waves in the outer 60 km. of the continental lithosphere as 5·8 km. per sec. Recent work upon the elastic constants and densities of rocks would go to show that at a depth of 35 km. the velocity in granite would be 5·9 km. per sec. Here there is evidently contradiction not only to the assumption of the existence of a peridotite layer immediately beneath the continents, but also to the shallow continents assumed by Dr. Jeffreys. Beyond 60 km., however, the velocity increases to 7·9 km. This—as Holmes points out (*loc. cit.* p. 531)—also agrees with the velocity given in Knott’s table.

There is, evidently, very slender evidence for the view that close under the granitic continents peridotite exists. The Oppau explosion-wave supports the view that “around Oppau the basaltic layer is in place beneath a depth of 30 to 35 km.” (A. Holmes, *loc. cit.* p. 531.) Holmes appears finally to favour the view, but not on any decisive grounds, that the basaltic layer is nowhere more than 42 km. thick, and that a peridotite layer of less radioactivity then begins. The radioactivity of peridotites and of the magma basalts differ a little, the calorific values being in the approximate ratio of 114 : 98†. And there is some reason to believe they are nearer to equality. The melting-points also seem generally to differ a little, that

\* Geol. Mag. Dec. 1925, p. 531.

† Phil. Mag. Nov. 1924.

of peridotite being the higher (it is difficult to say how much); but it is certain that the viscosity of the peridotites extends over a wider range of temperature than is the case with basalts. I have pointed out—more especially in my Halley Lecture (pp. 31–35)—the consequences which may arise from a deep-seated layer of peridotite.

Dr. Jeffreys next proceeds to combat the view “that periodic variation of temperature” arise within the crust; which he describes as my “main object.”

Now, this is not at all my main object. If Dr. Jeffreys had stated that my main object was to show that there is periodic accumulation and discharge of heat from within the crust he would be correct. But the heat is latent. There is but little variation in temperature. Throughout the rest of his argument he appears to labour under this initial error, and to assume that the problem he undertakes to discuss is concerned mainly with a periodic variation of temperature gradient; that is to say, the problem is one of thermal conductivity.

“There is,” he says, “no possibility of periodicity.” This is true of the mathematical theory of heat conduction. The periodicity which I have referred to in all my writings upon this subject arises from the gravitative instability which affects the ocean-floor when an underlying substratum assumes, in consequence of accumulated latent heat, the fluid state, and becomes of less density than the solid floor. The consequences arising out of this condition allow a very great transfer of latent heat by *convection* from the lower to the upper parts of the magma, so that the upward heat-flux during the fluid phase is very much greater than the mean, while the upward heat-flux during the solid phase is very much less than the mean.

The differential equation cited by Dr. Jeffreys is the same as that used by Mr. Cotter in his paper “On the Escape of Heat from the Earth’s Crust” (Phil. Mag. Sept. 1924), save that he assumes  $P$  (the rate of supply of heat per unit volume) constant. Of course the time enters through a negative exponential factor. The fact that Dr. Jeffreys thinks that the only way periodicity can arise is by a trigonometrical time factor in the expression for conduction, shows that he is under a misconception as to the conditions involved in the theory.

The analogue of the string damped by a viscous liquid is misleading. He supposes a barrier to limit the displacement of the string, just as the melting-point limits the rise of temperature of a solid. But he has nothing

analogous to the accumulation of energy in the form of latent heat. Also, there is nothing corresponding to the transfer of this energy by convection; i. e., the precipitation of solid basalt at the bottom of the fluid region accompanied by the melting away of the floor above. In his figure Dr. Jeffreys makes the temperature diminish with depth, just as the amplitude of vibration of a string diminishes towards the fixed end.

Following this, Dr. Jeffreys says that I adopt the view that fusion occurs below the ocean and below the continents, "but," he says, "not for any obvious reasons." This and the sentence which follows suggest that not alone is he under a misconception as to the nature of the theory in some of its most important aspects, but he has not entered quantitatively into the physical data brought forward where such are available. We are here, *inter alia*, informed that "the melting-points of rocks increase with their basicity; so oceanic rocks must, on the whole, have higher melting-points than continental ones." This is, however, inconsistent with the facts.

From my book (pp. 102-103) I am quoted as follows:—"If the substratum is solid, the radioactive heat continually being developed beneath the continents is almost entirely accumulated." "The blanketing effects of continental radioactivity... effectively block its escape by conductivity." Surely the meaning is plain enough; and is expounded many times throughout the book! Nevertheless, here is Dr. Jeffreys's comment:—"It seems to be supposed that heating a region prevents the transmission of heat through that region; which is not the case." We seem to have here the mathematical point of view with a vengeance. It is quite true that the linear character of the differential equation of heat conductivity suggests that a more correct way of stating the case would be to define that the flux of heat through the bottom of a continent is the algebraic sum of (a) the downward heat-flow from a radioactive continent into a non-radioactive substratum, and (b) the upward heat-flow from a radioactive substratum into a non-radioactive continent. I preferred, however, to take refuge in the second law of thermodynamics!

In the next paragraph Dr. Jeffreys seems to have become involved in a fresh difficulty. He says: "There seems no reason to believe that alternation between land and sea conditions will restore solidity." The restoration of solidity is not attributed to this, but to the precipitation of solid at the bottom of the fluid magma, together with



rise of superheated fluid magma which melts away the crust below the ocean-floor, thus transferring an enormous amount of (latent) heat by convection which escapes rapidly through the attenuated crust by conduction, and even by partial break-up of the ocean-floor. The temperature of the ocean waters remains, however, almost unaffected (*loc. cit.* pp. 98, 99).

Coming now to that part of Dr. Jeffreys's paper dealing with certain tidal effects which may be expected to arise upon the melting of the substratum, we find in his able treatment of this difficult subject a contribution to the surface history of the earth which, if confirmed, will have added considerably to our knowledge.

Dr. Jeffreys shows that conditions of depth of substratum as well as of its viscosity exert a controlling influence upon movements of the surface crust. That is, such movements as are to be expected as the effects of tide-generating forces acting upon the tidal prominences existing at opposite sides of the earth. He finds that, with the assumption of a depth of fluid substratum of 100 km. and favourable assumptions as to viscosity, an adequate displacement of the continents and ocean-floor over the substratal surface could be expected to take place only in some 50 million years. However, if the depth be taken as some 20 km. and the viscosity not greatly different from that giving the maximum tidal friction, it is possible that this part of the theory is self-consistent.

Of course the discussion applies to existing conditions of lunar proximity. Far greater tide-generating forces—according to Darwin's theory of lunar history—must have operated in the past, and very possibly affected the earlier terrestrial revolutions with which we are acquainted.

It would appear that the principal addition to our knowledge here involved is in the deduction that when solidification of the substratum is progressing, the shifting of the outer crust takes place effectively when the substratum has shallowed to a depth of about 20 km. Loss of heat will then have been in progress, according to my assumption as to its total effective depth, for a considerable time. This fact, as well as the pressure conditions, must influence the prevailing condition of viscosity which, however, we cannot determine, but which we are entitled to assume as favourable, having regard to what we know of geological history.

Even if we assumed that there were no other means

of equalization of thermal conditions beneath oceans and continents, it would appear that the crustal shift must ultimately account for complete equilibrium; for the gradual shallowing of the suboceanic depths must in itself involve continued approximation towards optimum conditions of crustal movement. This in turn involves progressive thermal equalization beneath continents and oceans, and thus introduces another accelerative factor. Plainly the results arrived at by Dr. Jeffreys involve an accelerative approach, slow at first, towards optimum conditions.

There are, however, other sources of magmatic circulation between sub-continental and sub-oceanic regions. Tidal movements must promote such circulation. I have referred to this in earlier papers upon this subject. Lateral currents have to feed the tidal prominences. Twice diurnally these movements occur; and as it seems probable that the greater, and less rigid, ocean-floor yields most to the tidal forces, very considerable movements drawing upon sub-continental magma may be expected to occur. Again, attending the slow sinking of the continents arising out of loss of magmatic density, a considerable transfer of sub-continental magma must continually be taking place.

Still another source of circulation, purely gravitational and arising out of the great vertical magmatic circulation beneath the oceans, seems to be inevitable. I refer to an attendant lateral circulation arising out of the gain in density of magma giving up latent heat to the ocean-floor. As this sinks downwards an upper lateral inflow of lighter material from beneath the continents will arise. At the lower levels compensatory magma, displaced by descending solidified basalt from above, flows from sub-oceanic to sub-continental regions.

A somewhat similar circulation takes place to-day in the oceans. We find, in fact, the cold waters of the Polar Regions spreading over the entire floor of the oceans. What is more, these currents extend over distances much in excess of the substratal circulation we have been considering; for it is known that the source of the cold bottom layer in the ocean is almost entirely of Antarctic origin, and penetrates to high north latitudes both in the Pacific and in the Atlantic. That such a great current exists is proved from the fact that, although exposed to sources of heat both above and beneath, the low temperature is

perennially maintained\*. This circulation is purely gravitational, and arises out of thermal changes of density. The circuit is closed through reverse surface currents and also by evaporation in the Tropics and precipitation in high latitudes.

We perceive, therefore, that while Dr. Jeffreys's conclusion leads us to a closer recognition of all the conditions, it raises no difficulties in the physical basis of the theory.

The grounding of compensations attending an east to west motion of the crust under tidal forces, towards closing stages of cooling, has been referred to by Dr. H. H. Poole as possibly affecting mountain-building (Phil. Mag. Sept. 1923). These effects would not be expected to interfere with crustal shifting at depths at all comparable with 20 km.—as Dr. Jeffreys suggests; for, in fact, mountain-genesis is, at this time, still in its earlier stages, and, of course, the compensations of a previous continental epoch will, to a large extent, have vanished. To-day we have to reckon with great compensations. But how much of these will remain in 30 or 50 millions of years? We have to bear in mind that it is an old and much denuded earth which the revolution assails.

When continental shifting finally ceases and tidal disturbances die out due to shallowing of the fluid substratum, there may remain, possibly, some local unconsolidated magma both under oceans and under continents. Slow escape by conductivity through the overlying crust accounts for such lodgments †.

I do not think we are faced with any difficulties in accounting for such depths of subcrustal fluidity as I have assumed. Lesser revolutions may arise out of lesser depths of liquefaction. Greater revolutions may arise out of greater depths of the substratum, and with these last the accumulated radioactive energy in a peridotite layer may be involved, as I have pointed out in my Halley Lecture. The new knowledge arising out of Dr. Jeffreys's analysis does not affect the available mountain-building forces and displacements attending a great revolution.

There is very striking geographical evidence for a westerly drift of the continents during some previous period of subcrustal fluidity. It is best seen where the westerly margin of the Pacific meets the easterly margin of Asia. Now, if the outer crust of the earth, retained

\* Supan, 'Grundzüge der Physischen Erdkunde,' p. 358.

† 'The Surface History of the Earth,' p. 95.

by lunar attraction, had moved from east to west relatively to the substratum, the sub-Asiatic substratum must have been displaced beneath the Pacific margin. The greatest continental stretch upon the globe lies to the west. If the molten substratum underlying this great continent was for ages being traversed by Eastern Asia and the adjacent Pacific floor, some evidence of exceptional thermal conditions might be expected.

Coming now to the geologic structure of this region, we find great slices of the Eastern Asiatic margin faulted downwards along step faults parallel with the coast and apparently conditioning the delimitation of the Japanese Islands. Many geologists consider the shallow Japanese Sea as due to foundering of an intermediate crustal area. Seaward we find the ocean-floor traversed by some of the greatest deeps on the globe. The whole region is continually shaken by earthquakes and by volcanic forces. It is to-day the most restless part of the earth's surface.

Now, foundering of continental land can only be explained in *one* way—having regard to isostasy—and that is by the melting away of underlying compensations. This view provides at once an adequate explanation. In this case the foundering of much of the fragmented coast and the buckled ocean-floor alike point to an area which had been undermined by extreme thermal conditions. Contrast with it the features of the eastern shores of the Pacific. There we find every sign of a strong ocean-floor. There is no continental fragmentation; the volcanicity and coastal oscillations are of different origin and are associated with mountain-building. There are no great deeps ranging along the continental margin. Nearly all the volcanic islands of the Pacific are in its western half. So are the fracture lines or rifts which seem to have determined the alignment of the Oceanic Islands.

The Atlantic offers no such remarkable conditions. There is a relatively small continental area lying to westward of the ocean. However, there were formerly highlands extending the east coast of North America into the Atlantic—highlands responsible for the enormous volume of sediment which built up the Appalachian Ranges. But ancient Appalachia for the greater part foundered long ago. There is no better attested case of foundering in geological history. We can assign the source if we reconstruct the past in the light of the radioactive surface history of the Globe.

LXXXIV. *The Sodium Arc in a Vacuum.* By F. H. NEWMAN, D.Sc., A.R.C.S., *Professor of Physics, University College, Exeter*\*.

[Plate XIV.]

1. *Introduction.*

THE spectrum lines emitted from any arc operated in a vacuum are very narrow, as distinct from the broadened and reversed lines given by the arc in air at atmospheric pressure. Unfortunately, with a number of substances the vacuum arc is intermittent even at potential differences as high as 200 volts. Rayleigh † has described a satisfactory type of sodium vacuum arc lamp made of silica in which the vapour is generated by the continuous heating of a pool of the metal forming the cathode, the anode being a tungsten rod. While working with a modified form of sodium arc lamp, it was found that under certain conditions the heat from the arc itself was sufficient to produce enough vapour for the discharge, no preliminary heating being required.

The main features of this lamp are shown in fig. 1. It is made of soda glass with windows at D and C. The cathode A consists of a pool of sodium metal in a glass tube, through the base of which passes the iron lead-in wire. A clearance between the outside of this cathode container and the inner wall of the lamp ensures that no sodium splutters to the glass walls. If this precaution is not observed, the arc passes by way of the spluttered sodium, and owing to the intense local heating developed, the glass invariably cracks. The anode B is an iron ring, so that the luminous vapour from the arc can be distilled away through the anode. There is a fair clearance between the latter and the glass walls, and no sodium can collect at this clearance. With these precautions it is possible continually to use the lamp without fracture, and such a glass lamp, which can be quickly constructed, is very useful as a source of sodium radiation. An auxiliary electrode E, enabling a momentary electric discharge from an induction coil to be passed between E and B, starts the arc. In actual practice the cathode A was cemented into a glass tube, which could be waxed on to the lower open end of the lamp, so that the sodium in the cathode container

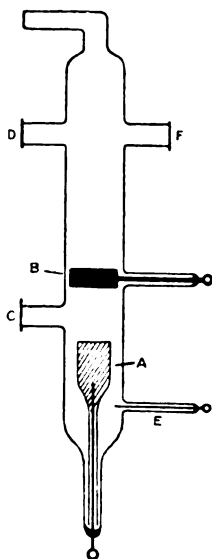
\* Communicated by the Author.

† Strutt, Proc. Roy. Soc. A. xcvi. p. 272 (1919).

could be easily and quickly replenished. This waxed joint was so far removed from the actual arc that it was not affected by the heat generated while the lamp was in operation.

The arc can be started by applying a potential difference of 90 volts between A and B, and then passing a momentary electric discharge between E and B. No heating is necessary, but asbestos cloth was wrapped around the lamp, as in the experiments made it was necessary to ensure that

Fig. 1.



the vapour which was being pumped away did not condense before it reached the window D. The current is regulated by a resistance, but the arc does not persist if the current falls below 1.5 amp., and it does not strike if the applied potential difference is less than 90 volts, although after the arc has been started the actual fall of potential across the electrodes is not greater than about 40 volts. No persistent arc could be obtained with the sodium as the anode. In the experiments the lamp was connected to a pump, running continuously, but a good vacuum is maintained while the arc is passing in the absence of the pump.

The spectra were observed and photographed by means of the constant deviation spectrometer.

## 2. *Experimental Results.*

When the arc is started the sodium vapour pressure is very low, and the radiation emitted is pink in colour. At this stage the luminosity is due to the current passing through the residual gases—chiefly nitrogen, hydrogen, and oxygen, and when examined through the window C the nitrogen bands are very prominent, as shown in spectrogram No. I. (Pl. XIV.). The most prominent lines are those constituting the first group of the positive bands, stretching from  $\lambda$  6878 to  $\lambda$  5754, the lines in the second group being extremely faint. The persistence of such a comparatively low voltage arc in the absence of an incandescent electrode is unusual, and must be explained by the small cathode fall of potential at the sodium electrode. It is well known that all of the alkali metals exhibit an abnormally low cathode fall.

Occasionally the whole of the lamp was filled with a brilliant blue "flash," and this luminous gas could be drawn along the tube from the arc, the luminosity persisting for 20–30 cm. along the tube. Unfortunately this "flashing" occurred spasmodically, so that its spectrum, and the conditions for excitation, could not be determined, but it is hoped to investigate the effect later.

After all of the air has been removed, and before the heat from the arc has become sufficient to produce any very appreciable amount of sodium vapour, a little hydrogen remains and is, in fact, extremely difficult to remove. At this stage the pressure within the lamp is very low, the glass walls showing green fluorescence under the action of the electric discharge. The arc discharge, viewed at C, shows a pink-coloured radiation which, when examined, is found to consist mainly of hydrogen lines—in fact, with the exception of  $\lambda$  5890,  $\lambda$  5896 from sodium, all the other lines are of the Balmer series, or of the secondary hydrogen spectrum, the outstanding lines being those constituting the first Fulcher band in the red. The second Fulcher band is very faint in comparison. The most intense lines are those in the three series  $S_1$ ,  $S_2$ , and  $S_3$ , the lines of these series decreasing uniformly in intensity as they extend towards the red end of the spectrum. This is shown in spectrograms No. II. and No. V. (Pl. XIV.), the latter being an enlarged photograph of the region  $\lambda$  6565– $\lambda$  5680.

It is well known that for a high relative intensity of the secondary hydrogen spectrum purity of the gas is essential, and this spectrum appears under less energetic conditions

of excitation than the Balmer series, the latter alone being found in vacuum tubes excited by powerful condensed discharges. Fulcher \* has shown that when hydrogen is excited by the impact of cathode rays, the relative intensity of the secondary spectrum increases as the velocity of the cathode rays is reduced, and the Fulcher bands are developed at these low potentials, the Balmer series lines becoming weaker. The bands are, as a rule, very faint in the presence of impurities, but in the present experiments the bands and the Balmer lines are both very intense in the presence of sodium vapour, although the amount of vapour must be minute at this stage, as the only prominent sodium lines are  $\lambda$  5896 and  $\lambda$  5890.

Kiuti †, using an arc at 400 volts between a tungsten anode and a cathode consisting of a bundle of tungsten filaments in an atmosphere of hydrogen at 2-3 atmospheres pressure, found that at high currents the lines of the secondary spectrum above  $\lambda$  5650 were intense. Fulcher, on the other hand, used only 40 volts, and Merton and Barratt ‡ state that the Fulcher lines are essentially low pressure lines, by which they indicate a pressure at which the walls of the vacuum tube show a vivid green fluorescence.

It has been inferred by various experimenters that the Fulcher lines between  $\lambda$  6000 and  $\lambda$  7000 originate in the same type of ionization of the molecule whether complete or partial. The predominance of the red bands over those in the second band suggests that the series in the first and second bands are not due to the same molecular system. On the other hand, in the present work, the series  $S_1$ ,  $S_2$ , and  $S_3$  are more highly developed than the remaining series in the first band— $S_4$ ,  $S_5$ ,  $S_6$ , and  $S_7$ . This seems to indicate a closer resemblance in origin between  $S_1$ ,  $S_2$ , and  $S_3$ , than exists between these series as a whole and the remaining series.

The bands undoubtedly belong to the arc type spectra, and it may be mentioned that in the first spectrogram the band spectrum of nitrogen alone is present. There is no trace of the arc or spark lines of this element.

As the arc in the sodium lamp continues the heat from it vaporizes the sodium. The spectrum of this element appears and becomes predominant as shown in spectrogram No. III. (Pl. XIV.), which was photographed through the window C. In fact, no lines except those belonging to the principal and

\* *Astrophys. Journ.* xxxvii. p. 60 (1913).

† *Phys. Math. Soc. Japan Proc.* v. p. 9 (1923).

‡ *Phil. Trans. A.* ccxxiii. p. 369 (1922).



the two subordinate series of sodium could be detected. Combination lines do not appear, but it must be remembered that the present experimental conditions do not favour the excitation of such lines. Although the D-lines are very intense the lines of the two subordinate series are bright, and it was found that if the current was decreased, i. e., as the temperature of the arc and the vapour pressure were lowered, the yellow radiation changed to a greenish colour before the arc was finally extinguished. This green-coloured radiation from the sodium arc has been observed by Rayleigh\*, but in his experiments it appeared at some distance from the arc. Its production evidently depends upon decreasing vapour pressure, but is difficult to explain on the atomic theory.

As the luminous vapour is distilled from the arc the luminosity persists for a considerable distance along the tube. The subordinate series lines, apparently, all lose intensity in the same ratio, but the D-lines are much less affected, as is shown in spectrogram No. IV. (Pl. XIV.), which was photographed at the window D. By having a small tube F opposite this window the effect of stray light was greatly minimised. This persistence of the D-radiation, as the vapour is distilled from the arc, may be due, partly, to resonance radiation stimulated by light from the arc itself, and incident on the sodium vapour as the latter passes along the tube. Rayleigh† has examined this persistence of radiation for various luminous vapours distilled from the arc.

LXXXV. *The Melting-points of the Normal Saturated Dibasic Acids.* By D. A. FAIRWEATHER, B.Sc., Ph.D., Chemistry Department, Edinburgh University ‡.

THE series of normal saturated dibasic acids has long attracted attention as furnishing a remarkable example of alternation in certain properties between the odd and even members. This effect is most pronounced in the melting-points of the acids: when these are plotted against the number of methylene groups in the chain, two smooth curves are obtained, one for the odd and one for the even members. A similar alternation is observed also in other

\* Strutt, 'Nature,' xciii. p. 32 (1914).

† Strutt, Proc. Roy. Soc. A. xc. p. 364 (1914).

‡ Communicated by Professor Sir James Walker, F.R.S.

homologous series, *e.g.* the monobasic fatty acids, whose melting-points rise steadily as the series ascends; the two curves lie close to each other, being separated by only a few degrees. In the series of dibasic acids, however, the odd acids lie upon an ascending curve, whereas the even ones lie upon a descending curve, *i.e.* the even acids have the unique property of continually decreasing melting-point with increasing molecular weight.

It has not hitherto been possible to determine with certainty whether or not the two curves cut each other, as the highest member of the even series previously available was hexadecanedicarboxylic acid,  $\text{HOOC} \cdot (\text{CH}_2)_{16} \cdot \text{COOH}$ , and many of the melting-points were not determined with sufficient accuracy\*. Four new acids higher in the series have now been prepared by Crum Brown and Walker's electrosynthetic method, namely those with twenty, twenty-four, twenty-eight, and thirty-two methylene groups†.

Following is a list of the melting-points of the even dibasic acids,  $(\text{CH}_2)_n \cdot (\text{COOH})_2$ .

	n.	m.pt.		n.	m.pt.
Succinic.....	2	185°	Hexadecane-		
Adipic .....	4	153°	dicarboxylic .....	16	124° (118°)
Suberic .....	6	140°	Eicosane-		
Sebacic .....	8	133°	dicarboxylic.....	20	123·75°
Decane-			Tetracosane-		
dicarboxylic ...	10	129° (127°)	dicarboxylic .....	24	123·5°
Dodecane-			Octacosane-		
dicarboxylic ...	12	126·5° (123°)	dicarboxylic .....	28	123·25°
Tetradecane-			Dotriacontane-		
dicarboxylic ...	14	125° (124°)	dicarboxylic .....	32	123°

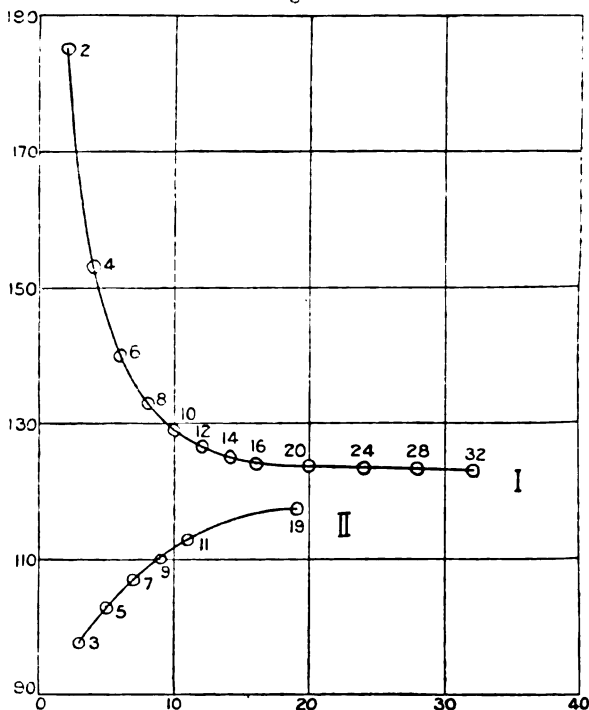
With the exception of the first four, whose melting-points may be taken as sufficiently well established, all these acids were prepared by the author in a specially pure state. The figures in brackets are the melting-points formerly attributed to these acids. In all cases the acids were purified by recrystallization from suitable solvents (chloroform or ethyl acetate) until no further rise in melting-point was observed. A standardized thermometer was used, and a correction for emergent stem applied, giving an error of less than ·25°.

\* Cf. Cuy, Journ. Am. Chem. Soc. 1920, p. 507.

† Fairweather, Proc. Roy. Soc. Edin. xlv. p. 283 (1925); xlv. p. 71 (1926).

In the diagram (fig. 1) the melting-points have been plotted against the number of methylene groups in the chain (I.). The corresponding curve for the odd series is also given (II.). The remarkable way in which curve I. flattens out after the point  $n=16$  has been reached is at once noticeable; there is, indeed, a difference of only one degree in melting-point due to the subsequent doubling of the hydrocarbon chain.

Fig. 1.



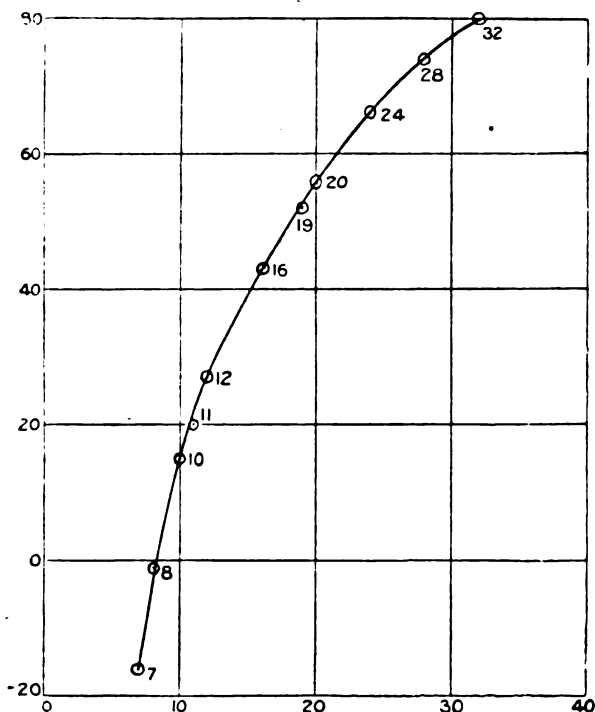
Melting-points of the dibasic acids:—I. even; II. odd. Vertical—m.pt. in degrees Centigrade; horizontal—no. of  $\text{CH}_2$  groups. The figures on the curve denote the no. of  $\text{CH}_2$  groups.

It has been observed that the most pronounced cases of alternation in homologous series occur (1) where there is a terminal polar group such as carboxyl, and (2) in properties involving the substances in the crystalline state, such as melting-points, heats of crystallization, solubilities, and molecular volumes\*. It is therefore probable that the explanation of such alternation is to be found in the crystal structure of the substances.

\* Garner & Ryder, Journ. Chem. Soc. 1925, p. 720. Garner & Randall, Journ. Chem. Soc. 1924, p. 881.

In the di-esters of the dibasic acids there is no terminal polar group, and the melting-points show no alternation whatever: they rise in quite a normal manner as the series is ascended, odd and even members alike lying on the same smooth curve (fig. 2).

Fig. 2.



Melting-points of ethyl esters of the dibasic acids. Vertical—m.pt. in degrees Centigrade; horizontal—no. of  $\text{CH}_2$ -groups. The figures on the curve denote the no. of  $\text{CH}_2$ -groups.

Following is a list of the melting-points of the diethyl esters of the dibasic acids,  $(\text{CH}_2)_n \cdot (\text{COOEt})_2$ .

Esters.	n.	m.pt.	Esters.	n.	m.pt.
Azelaic .....	7	-16°	Nonadecane-dicarboxylic .....	19	52°
Sebacic .....	8	- 1°	Eicosane-dicarboxylic .....	20	56°
Decane-dicarboxylic .....	10	15°	Tetracosane-dicarboxylic .....	24	66°
Undecane-dicarboxylic .....	11	20°	Octacosane-dicarboxylic .....	28	74°
Dodecane-dicarboxylic .....	12	27°	Dotriacontane-dicarboxylic .....	32	80°
Hexadecane-dicarboxylic .....	16	43°			

The melting-point given in the literature for diethyl sebacate ( $-4.5^{\circ}$ ) dated from 1876\*, and it was therefore thought advisable to verify it; no figure was available for diethyl azelate. Specimens of these two esters were accordingly prepared from the pure acids, and fractionated under reduced pressure. They were found to melt at  $-1^{\circ}$  and  $-16^{\circ}$  respectively. The esters of decane- and undecanedicarboxylic acids were similarly prepared and purified. The esters of eicosane-, tetracosane-, and octacosanedicarboxylic acids were purified by recrystallization from petroleum ether, and that of dotriacontanedicarboxylic acid from ether.

In order to explain the fact that malonic and glutaric acids give addition compounds with transchlorodiethylenediamine cobaltic chloride whereas oxalic, succinic, and adipic acids do not. Price and Brazier† have advanced the theory that the odd and even acids have different stereochemical structure, assigning the *cis* configuration to the odd acids and the *trans* to the even. Theories of this or similar nature, while perhaps offering an explanation of the existence of separate melting-point curves for the odd and even acids, by no means account for the lowering of melting-point with increase in molecular weight in the even series. We are led, in fact, to look for some peculiarity in the even series itself which does not exist in the odd or in any other known series.

The melting-point of a crystalline solid may be regarded as being largely determined by the magnitude of the forces of cohesion within the crystal‡. It has been shown that long chain compounds (hydrocarbons, fatty acids, and their esters etc.) have a tendency to arrange themselves side by side as in the monomolecular films obtained by Langmuir and by Adam, especially when pressed flat, the solid substance consisting of a large number of such layers superimposed upon one another§. The flakiness and greasiness of such compounds has been accounted for on this basis as being due to these layers slipping over one another||. Each layer of a compound having no terminal polar group has been found to be one molecule thick, but in the case of the fatty acids it is two molecules thick, the carboxyls being attracted to one another and lying in juxtaposition.

\* Neilson, Journ. Chem. Soc. 1876, p. 318.

† Journ. Chem. Soc. 1915, p. 1719.

‡ Bragg, 'X-rays and Crystal Structure,' 4th ed. p. 191.

§ Muller & Shearer, Journ. Chem. Soc. 1923, p. 3156. Muller & Saville, Journ. Chem. Soc. 1925, p. 599.

|| Bragg, 'Concerning the Nature of Things,' 1925, p. 196.

The half esters of the higher dibasic acids (*e.g.* ethyl hexadecanedicarboxylate,  $\text{EtOOC} \cdot (\text{CH}_2)_{16} \cdot \text{COOH}$ ) closely resemble the fatty acids (*e.g.* stearic acid) in their flakiness and greasiness, the two substances instanced being indistinguishable in these respects. The higher dibasic acids themselves, however, do not exhibit these properties in spite of their long hydrocarbon chains, but, on the contrary, are quite hard and brittle. Moreover, there is no reason to suppose that their chains are in any way different with respect to spatial arrangement from those of other chain compounds. This would seem to indicate that each is attached firmly at either end to the carboxyls of its neighbouring molecules. The major forces of cohesion which influence the melting-point would thus be those between the carboxyl groups.

The phenomenon under discussion would appear to be conditioned (1) by the presence of terminal carboxyl groups and (2) by the presence of a chain containing an even number of carbon atoms between them, and may be explained by assuming that the carboxyl groups exert some influence upon each other through the intervening chain. The nature of this influence, moreover, must be such that its transmission through an odd number of carbon atoms entirely alters its character.

As has been pointed out by Challenor and Thorpe\*, who were seeking an explanation of the greater chemical reactivity of the odd dibasic acids, the even acids have crossed polarities, *i.e.* the alternate positive and negative charges induced from the carboxyls at either end on each carbon atom of the chain tend to neutralize each other, whereas in the odd series they tend to reinforce each other. In the odd series, therefore, the mutual attraction of the carboxyl groups may be diminished by the presence of like charges upon them, in which case their melting-points would be lower than those in the even series. On this assumption the decrease in melting-point as the even series is ascended may be explained by the fact that as the chain is lengthened, the transmission of the alternate polarity effect is progressively weakened, and the terminal carboxyl carbons become gradually free from the influence of the carboxyl group at the other end of the chain. If this view were correct, it would be expected that when the chain became very long there would be little or no difference between the melting-points of consecutive odd and even acids. That this is indeed the case is very strikingly demonstrated in fig. 1,

\* Journ. Chem. Soc. 1923, p. 2482.

in which the two curves appear to approach each other asymptotically.

It has not so far been proved that the alternate polarity effect persists over a number of carbon atoms in a chain united by single bonds, but it is possible that cohesive forces in the crystals as measured by the melting-points constitute a more delicate means of detection of such an effect than has hitherto been used.

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LXXXVI. *Investigation of the Zirconium in Colorado Pitchblende.* By OLIVER FREE, B.A.\*

[Plate XV.]

THE study of this mineral was undertaken, since it is peculiar in being the only important uranium mineral stated to contain zirconium and because among the U.S.A. uraninites it is unique in being analogous to the Joachimsthal Pitchblende.

Following an extensive investigation of minerals containing uranium, W. F. Hillebrand (Am. J. Sci. xl. p. 384, 1890 ; xlii. p. 390, 1891 ; Bull. U.S. Geological Survey, lxxviii. p. 43) came to the conclusion that uraninites may be divided into two classes, primary and secondary, the first characterized by the presence of thorium and rare earths, the other by their absence. With the former group helium appears to be invariably associated, while in the latter it is present, if at all, only in minute quantities. Besides the chemical differences there is one of another kind, for probably all members of the first group occur in more or less well defined crystals, while those of the second group are generally, if not altogether, massive and free from crystalline form.

Hillebrand found that the Colorado variety occupied a somewhat anomalous position as regards the two groups. Its mode of occurrence and amorphous form, as well as the small percentage of helium, would point to its being a member of the second group, although it may be considered a member of the first group with zirconium in place of thorium and rare earths.

The identity of the constituent with zirconium was left by Hillebrand in some doubt, and the only test he recorded was that of turmeric paper, which produces a reddish-brown

\* Communicated by Professor F. Soddy.

colour when dried after being dipped in a hydrochloric acid solution of zirconium.

The primary uraninites of U.S.A. and Norway all contain a high percentage of lead, corresponding to the high percentage of helium. B. B. Boltwood (Am. J. Sci. xxiii. p. 85, 1907) showed how the age of radioactive minerals could be calculated from the lead-uranium ratio or from the helium-uranium ratio. The former gives a maximum age, while the latter gives a minimum. Boltwood did not take into consideration the fact that thorium as well as uranium produces lead and helium, although not at the same rate, so a new factor has now to be introduced. The conclusion remains unchanged if we consider a uranium mineral that does not contain thorium, as the Colorado Pitchblende.

Besides the anomalous position occupied by the Colorado Pitchblende with respect to the two classes of uraninites, it is interesting in the light of the discovery of hafnium, which resembles zirconium to a very marked degree, and makes it interesting to ascertain whether the element thought by Hillebrand to be zirconium was really zirconium or hafnium.

G. v. Hevesy and T. V. Jantzen (J. C. S. 123, p. 3221, 1923) state that it is well known, chiefly as a result of the measurements made by R. J. Strutt, that all zircons exhibit radioactive properties, by virtue of the presence in them of minute amounts of uranium or thorium. Zircons with large uranium or thorium contents were found to contain rather large amounts of hafnium, and the radioactivity of zircons accordingly show a rough parallelism with the hafnium content.

Since the Colorado Pitchblende contains zirconium in the presence of such a high percentage of uranium, it is therefore of interest to examine the zirconium for hafnium. The optical spectrum of hafnium has been carefully measured by H. M. Hansen and S. Werner (*Kgl. Danske Vid. Selskab Math.-fysiske Medd.* v. p. 8, 1923). The question may be settled either by means of the above optical spectrum lines or by density determinations. In a more recent paper G. v. Hevesy and V. Berglund (J.C.S. 125, p. 2372, 1924) give a density method for determining the ratio of zirconium to hafnium, using the density of their dioxides.

After a careful analytical study of the mineral with particular reference to the elements lead, uranium, thorium, rare earths, and zirconium, sufficient of the mineral was worked up for the zirconia for the density and the spectrum



to be determined. The uranium content was checked by radium estimations by the  $\gamma$ -ray and emanation methods. In addition to uranium as the main constituent, it contained water, silica, zirconia, iron, and a trace of lead, which were estimated. Traces of bismuth, tin, titanium, and vanadium were detected. Aluminium, thorium, and the rare earths were not found.

#### *Analysis of the Mineral.*

The specimen of Colorado Pitchblende examined was a single large block obtained from the Colorado-Gilpin, Gold and Radium Mining Company. A microscopic examination only showed the amorphous state of the mineral and the presence of an impurity of iron pyrites, which is shown by its cubic form with striations parallel to two of the edges.

The finely ground pitchblende was dissolved in strong nitric acid (1.42), the action being completed by warming. After dilution the insoluble residue was filtered off and freed from uranium by washing, finally ignited and weighed. The filtrate was then evaporated down to dryness with hydrochloric acid on a sand-bath. Part was rendered insoluble in dilute hydrochloric acid and this part, at first, was mistaken for soluble silica, but later was found to be mainly zirconia.

From the solution Group II. metals were separated with hydrogen sulphide. In minerals containing thorium and rare earths these are next removed by means of oxalic acid in a faintly acid solution. As all tests failed to detect either thorium or rare earths, this step was subsequently omitted.

The uranium was separated by pouring the solution into N/2 ammonium carbonate solution, and estimated chemically by the phosphate method of H. Brearley ('The Analytical Chemistry of Uranium,' 1903).

#### *Lead Determination.*

The proportion of lead is important as fixing the maximum age of the mineral and whether it is of primary or secondary origin. The amount of lead formed in one year from one gram of uranium is  $1.48 \times 10^{-10}$  gram. The age of the mineral is therefore given by  $6.75 \times 10^9 \text{ Pb/U}$ , where Pb/U is the ratio of the amount of lead to the amount of uranium in the mineral. The age of the Colorado Pitchblende as determined from the lead and the uranium contents as obtained by Hillebrand is approximately a hundred million years.

The Group II. sulphide precipitate was very small indeed, and a careful analysis of it showed it to contain principally lead with traces of bismuth and tin. For the estimation of the lead larger quantities of the order of 7.0 grams were used. The method used was to dissolve the well-washed sulphides in dilute nitric acid, add about 5 c.c. of dilute sulphuric acid and evaporate until white fumes are given off freely. After cooling, the residue is treated with 25 c.c. of water and 50 c.c. of alcohol, allowed to stand for some hours and filtered off through a Gooch crucible, which had been dried at a dull red heat inside a nickel crucible. The precipitate was washed free from sulphuric acid with alcohol and dried at a dull red heat as before. The mean of results gave  $0.0157 \pm 0.0017$  per cent. of lead. This gave the age of the mineral of the order of two million years.

It is interesting to compare this age with those obtained by Boltwood for the crystalline U.S.A. uraninites:—

Glastonbury, Conn. ...	410 million years.
Branchville, Conn. ...	530     "     "
North Carolina .....	510     "     "
South Carolina .....	460     "     "
Texas .....	1800     "     "

This result therefore proves that the mineral is of recent formation.

#### *Separation and Estimation of Zirconium.*

If zirconium was present in the mineral it would be precipitated with iron, etc., as a phosphate during the separation of uranium by the N/2 ammonium carbonate. Zirconium phosphate is very insoluble in acids, even more so than thorium, and the method of analysis makes use of this.

The separation of zirconium from iron, aluminium, and chromium was investigated by P. Nicolardot and A. Reglade (*Compt. Rend.* t. clxviii. p. 348, 1919). The method they employed was to separate as phosphate in a sulphuric acid solution. A 20 per cent. sulphuric acid solution was found necessary to retain all the iron in solution, but at the same time a little zirconium—less than 1 per cent.—was retained in solution.

The best method of precipitation was found to be from a hot dilute zirconium solution in 20 per cent. sulphuric acid by a hot solution of ammonium phosphate containing 10–100-fold excess, finally washing with a 5 per cent. ammonium nitrate solution.

The mixed phosphates were got into solution by fusion with sodium hydroxide and sodium peroxide (3 to 1) in a nickel crucible. After 30 to 40 minutes the melt was cooled and extracted with water. The insoluble residue, consisting principally of sodium zirconate and ferric hydroxide, was filtered off and well washed.

This method of fusion has the advantage not only of the use of a moderately low temperature, but it also makes a partial separation, for those amphoteric elements like aluminium pass into solution and are filtered off. Thus vanadium goes into solution as sodium vanadate and is thereby separated from titanium, which remains behind as sodium titanate. It is therefore possible to distinguish to which element the yellow coloration produced by hydrogen peroxide, in an acid solution, is due. It was noted that, after using a nickel crucible for two fusions, the zirconium became contaminated with nickel.

The residue of sodium zirconate after extraction with water was dissolved in 20 per cent. sulphuric acid to remove the iron. Heating facilitates the solution. Before adding the ammonium phosphate, a few drops of hydrogen peroxide were added in order to retain the titanium in solution as a pertitanate, which in dilute solutions is characterized by a light yellow colour similar to that produced by vanadium. The ammonium phosphate, equal to approximately  $1\frac{1}{2}$  times the weight of the mineral taken, was dissolved in 20 per cent. sulphuric acid before being added to the zirconium-containing solution. After boiling for a short time the precipitate was allowed to settle, then filtered off and washed with a 5 per cent. ammonium nitrate solution, dried, finally igniting and weighing as phosphate. The zirconium present is calculated as the dioxide.

The results of successive analyses were not concordant and search was made for zirconium in the insoluble residue.

#### *Examination of the Insoluble Residue.*

Part of the mineral insoluble in strong nitric acid amounted to some 8.75 per cent. This was treated with hydrofluoric acid, fumed with sulphuric acid, and ignited, and the loss in weight recorded as silica.

The residue left was found to contain zirconium, which was estimated as phosphate as before.

#### *Examination of the "Soluble Silica."*

On testing the precipitate, thought to be silica, obtained

by evaporating the acid solution of the mineral to dryness, by means of hydrofluoric acid, as above, only in one or two cases was there any loss in weight, and this was exceedingly small. The residue was found to be mainly zirconia.

The results show that there was 5.25 per cent. of zirconia in the mineral, 3.0 per cent. represents the portion separated from uranium as phosphate, 1.5 per cent. that remaining in the insoluble residue, and 0.75 per cent. that obtained as "soluble silica."

This was checked by another method of determination (U.S.A. Dept. of the Interior, Bureau of Mines, Bulletin 212). The powdered pitchblende instead of being dissolved in nitric acid was subjected to an alkaline fusion with sodium hydroxide and sodium peroxide, and the zirconium determined in the insoluble portion. The sodium zirconate was dissolved in hydrochloric acid, and through the boiling solution, after practically neutralizing with ammonia, was passed sulphur dioxide till saturated. The zirconium was precipitated as the hydroxide, which, after filtering and washing with 5 per cent. ammonium nitrate solution, was ignited and weighed as the dioxide. The mean value gave 5.5 per cent. zirconium dioxide.

#### *Determination of Iron.*

The iron was determined in the 20 per cent. sulphuric acid solution, after the precipitation of zirconium, by adding tartaric acid, precipitating as sulphide and weighing as oxide, as described by Treadwell and Hall (Analytical Chemistry, vol. ii.). From the microscopic examination it appeared that the iron was present chiefly as an impurity of iron pyrites, so the iron is calculated as  $\text{FeS}_2$ .

Vanadium was detected in the filtration obtained after extracting with water the melt from the fusion of the mixed phosphates. Addition of hydrogen peroxide to the acidified solution produced a faint yellow colour, and the same solution when reduced with sulphur dioxide gave the distinctive blue colour of the hypovanadate.

#### *Water Determination.*

The water was determined by heating the finely ground pitchblende in an air oven at  $110^\circ$  until a constant weight was obtained.

*Uranium Estimation.*

The chemical method for determining uranium as phosphate as described by Brearley requires practice, as a considerable loss is experienced during the successive filtration owing to the difficulty of washing the filter free from all traces of uranium. The three final determinations gave the following values: 66.5 per cent., 65.0 per cent., and 66.9 per cent. of uranium element. In the calculation of the percentage of  $U_3O_8$  the middle value was omitted, since the other two agree more closely with the value obtained by the emanation method.

*Radioactive Estimation. The  $\gamma$ -Ray Method.*

The uranium content of the mineral was compared with that of minerals of known uranium content by the  $\gamma$ -ray method, and correcting for the absorption of the  $\gamma$  rays by the mineral (F. Soddy, 'Chemistry of the Radio Elements,' 1915). These indicated the percentage of uranium as between 61.3 per cent. and 70.08 per cent., but the method was abandoned as not giving sufficiently concordant results.

*The Emanation Method.*

In preparation for this measurement about 0.2 gram of the Colorado Pitchblende was dissolved in a few c.c. of nitric acid, and amounts corresponding to 2.0 mg. of the original mineral were sealed up for a month and the emanation determined in the usual way by means of an emanation electroscope. The electroscope was standardized by emanation from a known quantity of radium, and a leak of one division per minute corresponded to  $32.4 \times 10^{-12}$  gram of radium.

The value first obtained was approximately 60.0 per cent. of uranium element, which was below all the chemically-determined values. It was thought that it was probably due to some of the radium remaining in the insoluble residue. The above experiment was repeated as before, only in this case the insoluble residue was first treated with hydrofluoric acid, fused with fusion mixture, and the melt dissolved in hydrochloric acid and placed in a separate emanation flask. After a month the emanation in the new flasks was measured, and found to correspond to 63.2 per cent. and 3.8 per cent. of uranium element respectively, making a total of 67.0 per cent. of uranium element, in good agreement with the final chemically-determined value.

The probable composition of the Colorado Pitchblende a

given by the mean values of the various analyses is as follows :—

U <sub>3</sub> O <sub>8</sub> .....	78.9 per cent.
FeS <sub>2</sub> .....	6.7
SiO <sub>2</sub> .....	5.9
ZrO <sub>2</sub> .....	5.25
H <sub>2</sub> O.....	1.75
Residue .....	1.2
Traces of other elements ...	0.2
Total.....	99.90 per cent.

### *Preparation of Zirconia in Quantity.*

Approximately 45 grams of Colorado Pitchblende were worked up for the separation of zirconium in order that the density determinations and the optical spectrum might be obtained.

Quantities of the order of 6 grams were dissolved in concentrated nitric acid. The solution was then evaporated down to dryness with previous addition of hydrochloric acid. The residue was then treated with dilute hydrochloric acid, and the insoluble part filtered off. The excess of acid was practically neutralized before pouring into the N/2 ammonium carbonate solution.

The zirconium was separated in exactly the same manner as described above. In working with the large quantities of zirconium difficulty was experienced in washing the phosphate free from iron during the filtration. Four successive fusions and precipitations were necessary to free the zirconium from iron.

The zirconium was extracted from the insoluble residue by an alkaline fusion without previously treating with hydrofluoric acid, and was kept separate from the rest.

In addition to the zirconium from the Colorado Pitchblende, two other zirconium preparations were prepared for the purpose of comparison. One preparation being from a blue Natural Zircon (Siam), reputed to be rich in hafnium, the other was a Commercial Hydrated Zirconium Oxide.

### *Density Determinations.*

G. v. Hevesy and V. Berglund (J. C. S. 125, p. 2372, 1924) have found that the density of the mixed oxides of hafnium and zirconium could be regarded as a linear function of the composition, and used this method for

determining the percentage of hafnium present. The density of the pure dioxides of both elements was first determined. The two elements had first to be separated by a fractional crystallization of the double potassium fluoride. The mean values they obtained at  $20.0^{\circ}$  were  $\text{ZrO}_2$ , 5.73;  $\text{HfO}_2$ , 9.67. The density of the mixed oxide being known, the percentage of hafnium dioxide was calculated by means of the formula

$$x = \left( \frac{d - 5.73}{0.0394} \right),$$

where  $d$  is the density of the mixed oxide at  $20.0^{\circ}$ .

The method of preparing the oxide after the necessary purification of the zirconium phosphate was to remove the phosphoric acid by means of an additional alkaline fusion, the sodium zirconate was dissolved in dilute sulphuric acid and precipitated as the hydroxide with ammonia, and washing free from sodium with a 5 per cent. ammonium nitrate solution. The hydroxide was then transferred to a platinum dish and dissolved in concentrated sulphuric acid, the excess of the latter was driven off on a sand-bath until dryness was obtained, and the remaining acid was expelled at a dull red heat. The final heating at  $1000^{\circ}$  was done in an electric furnace. The heating was continued until a constant weight was obtained.

The density of the four oxides was obtained by using a specific gravity bottle of 10 c.c. capacity. The bottle was filled with air-free distilled water in a vacuum desiccator, evacuation being continued until no more bubbles of air arose. The bottle and contents were hung for one and a half hours in a thermostat maintained at  $20.0^{\circ}$ .

Five determinations of each specimen gave the following values :—

Colorado Pitchblende :

Portion soluble in  $\text{HNO}_3$  ..... 5.133

Portion insoluble in  $\text{HNO}_3$  ... 5.278

Siamese Zircon ... ..... 5.165

Commercial Hydrated Oxide ..... 5.152

These values are lower than those given by Hevesy for  $\text{ZrO}_2$ , but they are probably comparable among themselves as an indication of the hafnium content of the four specimens. They show that it cannot be widely different, and it is most probable that hafnium is there only in very small quantities.

It is hoped to have the above specimens subjected to an X-ray analysis, the results of which will be communicated as soon as possible.

*Spectroscopy.*

To obtain the photograph of the spectra a Féry spectrograph was used, thereby six spectra can be photographed on one negative. Photographs were taken of the four zirconium spectra together with those of the carbon and iron arcs. The latter was used as a standard for calculating the wave-lengths of the required lines.

The negative was projected and the enlarged image examined. Many lines were seen in the zirconium from the Colorado Pitchblende that were not in the other two spectra. Those regions where lines of interest were located were then printed. The wave-lengths of the various lines were calculated by reference to the iron arc standard. All the zirconium lines as given by Exner and Haschek (*Sitzungsb. kais. Akad. Wiss. Wien*, cvii. Abth. IIa. p. 825; *Wellenlängen Tabellen der Bogensp. der Elemente*), and reproduced by W. Marshall Watts ('Index of Spectra,' Appendix T), in these regions, were found in the spectra of the preparations from the Colorado Pitchblende, which thus established the identity of the constituent with zirconium.

From the wave-length of the unknown lines, nickel was suspected as an impurity, and upon comparison with a nickel spectrum this was found to be correct. At the same time it should be pointed out that only the very prominent nickel lines showed, and were strongest in the region between 2350 Å.U. and 2310 Å.U., where some fifteen lines were identified. In Pl. XV. the nickel lines are not sufficiently strong to show. The nickel lines were strongest in the portion of zirconium that was soluble in nitric acid.

In addition a group of lines of wave-length : 2545·3, 2552·5, 2555·9, 2560·4, and 2563·3 Å.U. were observed, and then, on reference to Kayser ('*Handbuch der Spectroscopie*'), were found to agree with scandium lines. The presence of scandium was confirmed by comparison with the spectrum of a scandium preparation kindly supplied by Professor Morgan. It may be recalled that Sir W. Crookes (*Phil. Trans. A*, ccix. 1909) found scandium closely associated with zirconium in minerals.

The spectra over the regions examined showed no lines, except those of nickel and scandium, not given in the spectrum of zirconium as recorded by Marshall Watts. Several of these are given by Hansen and Werner as due to hafnium, but it is impossible to say with certainty that the lines were actually those of hafnium, since the observed intensity did not agree with those given by Hansen and Werner, nor was there a constant variation.



Plate XV. shows, from left to right, the spectra: (1) a mixed zirconium and nickel preparation, (2) zirconium from Colorado Pitchblende ("soluble silica"), (3) zirconium from Colorado Pitchblende (part soluble in nitric acid), (4) and (5) short and long exposures of scandium oxide, and (6) the carbon arc alone. The magnification is 12.5 times the original negative. The markings in the left-hand gap indicate the position of the zirconium lines as given by Marshall Watts, those in the right, the scandium lines. The scale is graduated in 0.5 Å.U. per division, and acknowledgment is made to Professor Soddy for permission to make use of his calibrated spectroscope and these hitherto unpublished methods for the identification of the spectrum lines.

### *Summary.*

An examination of the pitchblende from Colorado has been made. The lead-uranium ratio was very small and indicates a maximum age of two million years. This establishes the recent formation of the mineral in contradiction to the other U.S.A. uraninites examined by Hillebrand and Boltwood. The identity of the constituent thought by Hillebrand to be zirconium has been confirmed, and no thorium or rare earths could be detected in the mineral.

The chemical and radioactive analyses of the mineral gave 78.9 per cent.  $U_3O_8$ , 5.25 per cent.  $ZrO_2$ , with silica, pyrites, and moisture as the important constituents, and traces of lead, titanium, and vanadium.

A comparison of the density of the zirconia separated from large quantities of the mineral with specimens of zirconia separated from a blue Siamese Zircon, reputed to be rich in hafnium, and with a commercial zirconia preparation, showed that all these specimens were of similar low density and therefore of similar low hafnium content. The spectra of the preparations were also similar, and give no evidence of any differences in hafnium content. In the spectra of the specimens from the pitchblende the scandium lines were very clearly shown.

The author's best thanks are due to Professor F. Soddy for suggesting and directing the above research.

The Old Chemistry Department,  
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LXXXVII. *The Scattering of Positive Rays by Hydrogen.* By  
G. P. THOMSON, M.A., *Fellow of Corpus Christi College,  
Cambridge, and Professor of Natural Philosophy in the  
University of Aberdeen* \*.

[Plate XVI.]

**I**N an earlier paper † an account was given of measurements made on the scattering of positive rays from hydrogen in hydrogen gas. The results were not such as could be explained on the assumption of the inverse square law of force acting between the protons and electrons. The rays in these first experiments were measured by passing them through a slit of variable width into a Faraday cylinder and observing the rate at which it gained charge. This method is not entirely satisfactory for two reasons ‡.

In the first place, the positive rays are continually gaining and losing their charges during their passage through the scattering gas, and it is not certain that the proportion of charged to uncharged rays is the same in the scattered and unscattered portions of the beam. Indeed, as was pointed out in the above mentioned paper, one would expect the scattering, as observed by this method, of molecular rays, which are probably dissociated in the process, to be about half its true value. Secondly, the electrical method, at least in the form used, is not an accurate way of measuring scattering through angles such that the scattered rays are a very small fraction of the total, and it was not found possible to deduce a collision relation from the data obtained.

For these reasons the earlier experiments were considered as giving only the order of the effect, and it was thought best to make further experiments by another method. That chosen was to compare the blackening caused in a photographic plate by the scattered and unscattered portions of a beam of positive rays which were allowed to strike it.

*Apparatus.*

After some preliminary experiments with unanalysed rays, the apparatus shown in fig. 1 was adopted. The rays generated in the discharge-tube A, pass through two slits B in the cathode C. The slits were of the types used by Aston, and were 19 mm. wide and 3 mm. across. The

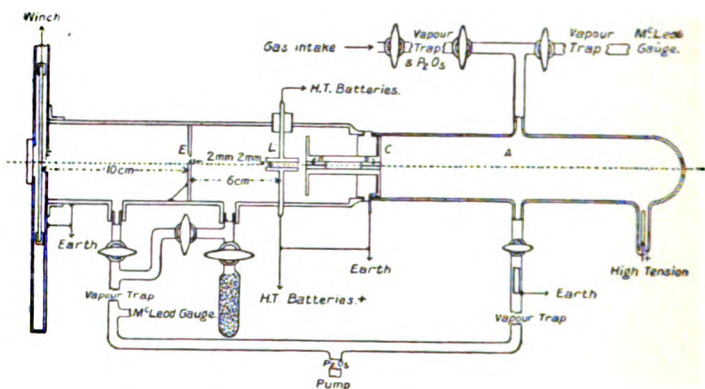
\* Communicated by the Author.

† Proc. Roy. Soc. A. cii. p. 197 (1922).

‡ For a correction to the calculations in this paper, see p. 973 (note).

rays then passed between the plates of the condenser L, where they were deflected by an electric field caused by connecting one of the plates of L to the terminal of a battery, the other terminal and plate being earthed. The rays thus spread into an electric spectrum of which a portion was selected by the aluminium slit E, .5 mm. wide. They then passed through the scattering gas and struck the plate F. This plate could be raised and lowered by means of the usual winch, and several exposures could be taken in rapid succession on the same plate, one above the other.

Fig. 1.



The connexions to gas-holder, pump, and gauges were as shown, and a constant stream of hydrogen, made by the electrolysis of caustic soda and dried with phosphorus pentoxide, was passed through the apparatus. Mercury was carefully excluded by means of traps cooled in liquid air, and the scattering vessel was in connexion with charcoal cooled in liquid air to further purify the hydrogen there.

To obtain the necessary relation between the number of rays and the blackening a series of photographs was taken, each time with varying exposures, the scattering being measured only on the blackest. A typical plate is shown in Pl. XVI.\*

As only an electrical separation of the rays was used

\* A peculiar effect is shown on practically all the plates. The edges of the strip due to the main beam are appreciably darker than the centre. This is not due to dirt on the slit, which was always very carefully cleaned. It occurs with slits of brass, brass gilded, and aluminium. It is proposed to investigate this effect further.

*Note added in Proof.*—It now appears that this is an optical delusion of a very persistent type.

these consisted of both atoms and molecules, and it was necessary to allow for this in analysing the results. To do so, an extra exposure was made on each plate (seen at the top in Pl. XVI.) with a magnetic field (not shown in fig. 1) applied just behind E in a direction to give a displacement opposite to that due to L. This will be recognized as a simple form of Aston's mass spectrograph, and gives a line on the plate for each type of ray present. As the pressure in the scattering chamber is high, there is a good deal of "secondary" present seen in the Plate as diffuse illumination, but there was no difficulty in allowing for this in the measurements and determining the proportion of atoms to molecules present. This varied from near equality in one case to cases in which the molecule was so faint in relation to the atom that it could hardly be seen, and measurements were impossible.

### *Measurements.*

The measurements of blackening were made by a selenium cell density meter of the type designed by Messrs. Toy & Rawlings\* and made by Watson. This instrument compares densities against those of a standard neutral wedge, and was found very satisfactory.

The following scheme was based on methods used in measurements of the speed of plates. The density of the centre of the pattern was plotted against the logarithm of the exposure time in seconds. This gave a curve, which, in agreement with results obtained for plates acted on by light, showed a straight portion over the region of normal exposure. For very small exposures the blackening was a little more than would be given by producing the straight line, while for over-exposure it grew increasingly less. This curve was then used to translate the measured densities of the scattered rays in the long exposure, into the corresponding intensities of rays. Thus supposing the exposure for scattering was 10 min., and it was found that the blackening at a particular place in the scattered region was the same as that of the centre strip in an exposure of 20 secs., the intensity of the scattered rays is taken as  $\frac{20}{600} = 3.3$  per cent. of the main beam. This assumes, (1) that the intensity of the rays does not alter during the exposure, (2) that the blackening depends only on the total number

\* *Journal of Scientific Instruments*, i. p. 363 (1924).

of rays striking a small portion of the plate, and not on the length of time of the exposure. The first assumption was checked by having the first and last exposure of equal times and rejecting all plates on which their blackening differed to an appreciable extent. The second assumption is rendered probable by the fact that the rays are quite separate entities striking at random. The corresponding law for light has been shown by Schwarzschild not to be strictly true, but even here the divergence is not very great. A similar effect in our case would make a difference to the absolute values obtained for the scattering, but very little to the relative scattering through different angles and for rays of different speed. It should be noticed that the above method of reduction applies equally well even though the centre strip of the exposure measured for scattering is much over-exposed. The measurements were taken only on one side (below) the central strip, this is because the part above is liable to have its blackening increased by rays scattered from the undeviated beam, which of course always exists, and in fact this region is always somewhat blacker than the corresponding point on the other side.

#### *Photographic Effect of the Rays.*

The plates used were Paget Process plates, and they were developed for 2 min. at 65° F. in the standard hydroquinone developer recommended by the makers. To secure uniform development the developing tank described by Dobson \* was used. The plates were fixed for 1 min. in acid hypo, washed and dried.

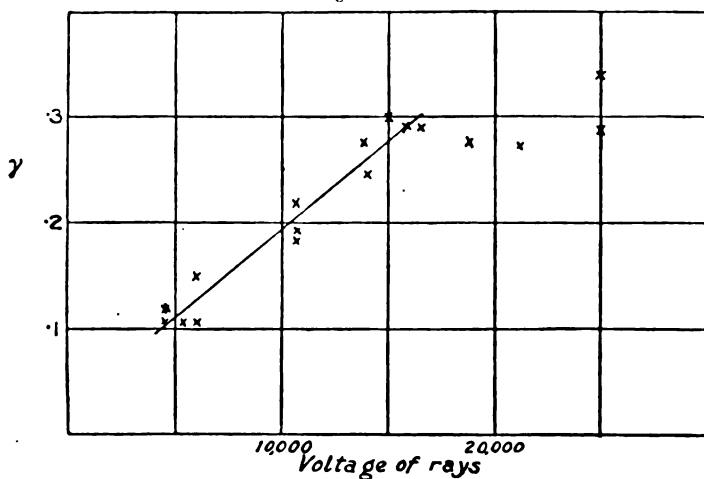
It is of interest to compare the law of blackening of these plates for positive rays with that for light. As mentioned above, the shape of the curve connecting density with the logarithm of the exposure was similar in the two cases. The slope of the straight portion of this curve is the quantity called  $\gamma$  in measurements of the speed of plates. Fabry and Buisson † have developed a theory, which seems to be borne out by experiment, according to which  $\gamma = \frac{m'}{m}$ , where  $m$  is absorption coefficient of the sensitive film for the exciting light, and  $m'$  the same quantity for the blackened film, and the light used to measure its density. Thus comparisons of  $\gamma$  under similar conditions of measurement should compare the penetrating power of the rays, and the agreement in the

\* 'Nature,' cxiv. p. 752 (1924).

† *Journal de Physique et le Radium*, v. p. 97.

shape of the curve with that found for light suggests that the absorption of the rays like that of light is roughly exponential. Fig. 2 shows  $\gamma$  plotted against the energy of the rays. It will be seen that the relation is a linear one up to an energy of 16,000 volts, after which  $\gamma$  seems to be nearly constant, perhaps owing to the rays going through the whole of the sensitive film. The measurements here, however, are less reliable as the values taken for the exposures did not allow the straight portion of the curve to be drawn with such accuracy as at the lower energies.

Fig. 2.

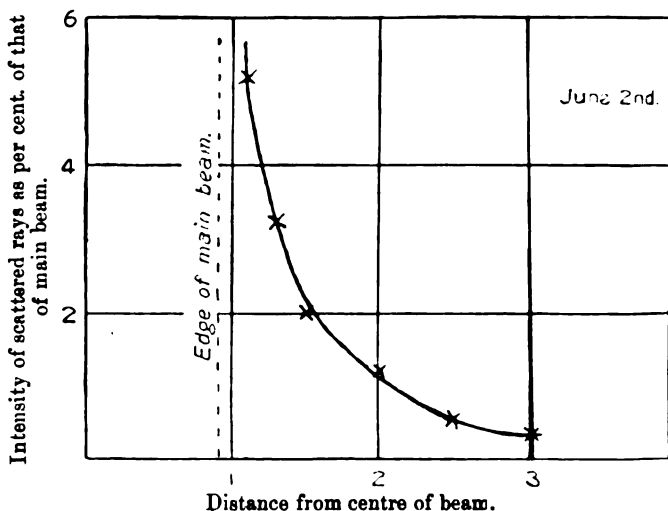


The increase of  $\gamma$  with penetrating power is no doubt the explanation of the results obtained by Aston with Schumanised plates. These plates have the silver bromide concentrated in a very thin layer near the surface, and Aston finds them especially effective for recording the heavier rays. For ordinary plates  $\gamma$  is probably small for these rays owing to their slow speed, which must decrease their penetrating power. Consequently it is almost impossible to get a black negative from them even with prolonged exposure. By using plates with a thin film  $\gamma$  is increased and the conditions are more like those obtaining with hydrogen rays in the ordinary plates. This point is of importance in connexion with the possibility of using methods similar to the above to determine the relative proportions of isotopes, as for such a purpose  $\gamma$  must not be too small.

*Reduction of Results.*

The measurements obtained give a curve of which fig. 3 is an example connecting the intensity of the scattered rays at a given place with the distance of the place from the centre of the beam of rays. The first stage in the reduction is to deduce from this the corresponding relation which

Fig. 3.



would hold if the beam were an infinitely narrow one instead of being, as it is, of an angle of about  $2^\circ$  giving a width on the plate of 1.8 mm. The beam can be regarded as approximately of uniform intensity over this width, and the following argument then applies. Let  $2a$  be the width of the beam at the plate and  $N$  the total number of rays per sec. in it. Suppose that a fraction of the rays  $f(x)dx$  be scattered through a distance on the plate between  $x$  and  $x + \delta x$ . Then the density of scattered rays at a point  $\xi$  from the edge of the main beam is

$$\phi(\xi) = \frac{N}{2a} \int_{\xi}^{\xi+2a} f(x) dx = \frac{N}{2a} \int_{\xi}^{\infty} f(x) dx - \frac{N}{2a} \int_{\xi+2a}^{\infty} f(x) dx.$$

Now in practice  $f(x)$  decreases fairly rapidly with  $x$ , and it follows that

$$\frac{N}{2a} \int_{\xi}^{\infty} f(x) dx = \phi(\xi) + \phi(\xi+2a) + \phi(\xi+4a) + \dots$$

if the series is convergent, as it must be in practice.

Thus the measurements of blackening give the fraction of rays scattered through a distance greater than  $\xi$ .

A difficulty arises in applying the above result as the scattering decreases rapidly with increasing distance from the beam, and becomes too small to measure at a distance of a few mm. Thus not more than two terms of the series can be determined experimentally. Though the blackening further out is too small to measure with any accuracy, the corresponding terms in the series may make an appreciable difference to the value of  $\int_{\xi}^{\infty} f(x)dx$ . The only way of evaluating them is by assuming a mathematical expression for  $\phi(\xi)$ .

It was shown in the paper referred to above that, assuming the scattering forces followed the inverse square law,  $\phi(\xi)$  varies as

$$\frac{1}{\xi^2} - \frac{1}{(2a + \xi)^2}.$$

It was apparent from the first that this was not the case in these experiments. An expression more in accordance with the facts is

$$\phi(\xi) \propto \frac{1}{\xi} - \frac{1}{2a + \xi} \quad \text{corresponding to } f(x) \propto \frac{1}{x^2},$$

but even this differed from the observations by more than the errors of experiment. If  $f(x)$  is taken as varying as a power of  $x$  the approximate value of the index is  $-1.7$ . The divergence from the expression

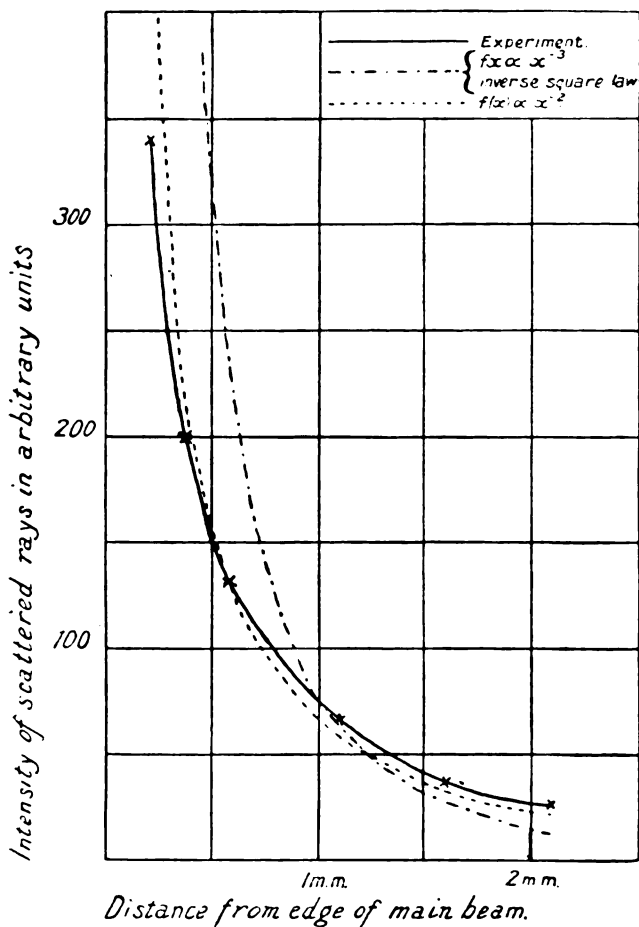
$$\phi(\xi) \propto \frac{1}{\xi} - \frac{1}{2a + \xi}$$

is, however, small except for values of less than .3 mm. for which the scattering is appreciably less than given by the expression. As will be seen in the next paragraph the scattering very close in may be produced in a different manner, plural scattering, from that further out which is single, and it therefore seems best to neglect the measurements close in; the rest agree well with the law  $f(x) \propto \frac{1}{x^2}$ .

The form of the function did not seem to vary with the energy of the rays, and fig. 4 shows the mean value for fourteen experiments compared with two calculated curves.



Fig. 4.



### *The Nature of the Scattering observed.*

A point of fundamental importance in the interpretation of any experiments on scattering is to determine whether the scattering is "single," "plural," or "multiple," i. e. whether the bulk of the scattered particles are deflected by only one effective collision, by a small number, or by many. The last possibility can be ruled out for two reasons. It would lead to an error curve for the distribution of the scattered rays which is quite contrary to what is observed, and it is incompatible with the known size of the molecule

as given by kinetic theory arguments. For a pressure of 6/1000 mm., which was not exceeded except for the measurements made to determine the variation with pressure, the total target area per sq. cm. of the hydrogen molecules in the 16 cm. over which scattering took place is 1.28, using Sutherland's value  $2.17 \times 10^{-8}$  for the diameter of the hydrogen molecule, thus the most probable number of collisions is one.

To distinguish between single and plural scattering is more difficult. Wentzel\* has developed an elaborate theory, which, however, requires a knowledge of the collision relation to apply it. As I wish to avoid assumptions as to this at the present stage the following argument is used, which is based only on the observed shape of the scattering curve, and the assumption that the total number of collisions producing detectable scattering is not more than would be deduced from kinetic theory considerations taking the proton as a point. It can easily be shown, assuming the experimental result that  $f(x) \propto x^{-2}$ , that, if  $n$  be the fraction which at one collision is turned through an angle greater than  $\epsilon/l$ , where  $l$  is the length of the scattering chamber, the fraction which is deflected by one collision through a distance on the plate greater than  $\epsilon$  is  $n/2$ .

Now choose  $\epsilon$  so that the fraction observed to be scattered through more than  $\epsilon$  is 10 per cent. If plural scattering is taking place the number scattered through this distance by one collision only will be less, so we are on the safe side. Now if  $\mu$  is the chance per unit of path of a deflexion more than  $\epsilon/l$ , the fraction  $n$  making one such collision and one only is  $\mu l e^{-\mu l}$ . Hence  $\mu l e^{-\mu l} \geq .2$ . Treating this as an equality we find  $\mu l = .26$  or  $2.55$ ; the latter solution can be neglected from the above kinetic theory considerations, thus  $\mu l < .26$ . The number with two or more such collisions is  $1 - e^{-\mu l} (\mu l + 1)$ , which is less than .028 or less than  $\frac{1}{4}$  of those with one only. We may neglect this fraction to the order of accuracy of the experiments.

There remains the possibility that there may be enough collisions giving deflexions of less than  $\epsilon/l$  to produce an appreciable effect. Here we return to the kinetic theory considerations. In the case mentioned before it may be shown that .35 make one collision only and .228 make two only, .138 making more than two. Now if we only consider places outside  $2\epsilon$  the first two classes cannot contribute, unless their individual deflexions are each greater than  $\epsilon/l$ , the case we have already dealt with. Of the remainder

\* *Ann. d. Phys.* lxi. p. 335 (1922).

those which make just three collisions are the most numerous and are .098 of the total. Now  $\frac{3}{4}$  of these will have two deflexions one way and one the other, so that even in the worst possible case in which all had three single deflexions only slightly less than  $\epsilon/l$ , only .025 would have a deflexion on the plate of  $2\epsilon$  or more, even if all three collisions took place at the beginning of the path where they would give the biggest displacement on the plate. The collisions are really uniformly distributed over the path through the scattering chamber, and considerations similar to those in the case of single scattering show that the number is approximately halved. Thus .012 is approximately the number which may have more than  $2\epsilon$  deflexion due to plural scattering. Now due to single scattering .1 have deflexions more than  $\epsilon$  and following the observed law .05 will have more than  $.2\epsilon$ . This is four times those due to plural scattering. Thus we have the following conditions to ensure that the scattering shall be predominately single. Take the distance such that 10 per cent. of the rays are scattered beyond it. Then at twice this distance, i.e. where the scattering is 5 per cent., the plurally scattered rays are in a minority of at least 1 in 4, and it is easy to see that their proportion rapidly diminishes further out. Beyond this place then, we have effectively single scattering provided the pressure is not greater than 6/1000 mm. In the experiments considered in this paper the above conditions were always satisfied for distances on the plate greater than .4 mm. and usually for considerably smaller distances.

#### *Variation of Scattering with Pressure.*

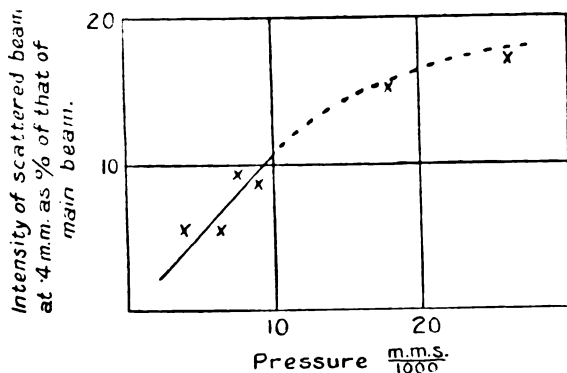
As a check on the above argument a number of experiments were made to determine how the scattering varied with the pressure of the scattering gas. The pressure in the discharge-tube was kept fairly high so that practically all the rays were atomic. The results are shown in fig. 5 plotted against the pressure. The scattering is measured at .4 mm. from the edge of the main beam. It will be noticed that when the scattering is more than about 10 per cent. it increases much more slowly than in proportion to the pressure, showing that the scattering is becoming plural, as might be expected from the above. The pressures also are higher than 6/1000 mm.

The straightness up to this point suggests indeed that the conditions stated in the last section are unnecessarily severe, which is also borne out by the fact that the shape of the

scattering curve shows no appreciable change for these points.

The scattering at small pressures can be taken from the slope of the straight portion of the curve. The energy of the rays did not vary much in these experiments and averaged 5000 volts.

Fig. 5.



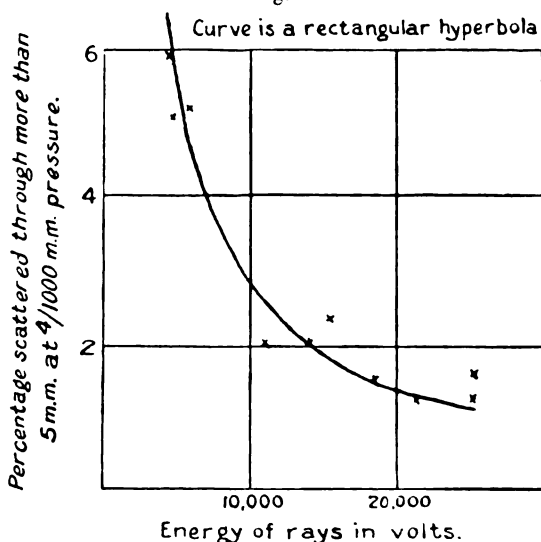
### Variation of Scattering with Energy of the Rays.

If the scattering is measured under the conditions of single scattering and reduced to a standard pressure, the way in which it varies with the energy of the ray can be determined. If we may assume that the internal motions of the parts of the molecule are not an important factor, and that the forces are independent of the relative velocity, there is a simple relation connecting the variation of scattering with energy with the function we have called  $f(x)$ .

In practice the angles through which the rays are scattered are small, and the angular deviation produced in a ray passing through a given field of force is inversely as its energy  $E$ . Now suppose the complete expression for the fraction of rays scattered through a distance between  $x$  and  $x + \delta x$  is  $\psi(E, x) dx$  at a small standard pressure. This fraction is the number that pass through a particular portion of the field of force of the scattering molecules, and since the paths of the rays are not appreciably shifted by the small deviations they experience, this number will be the same whatever the energy of the rays. The corresponding deflexions, however, are inversely as  $E$ , and it follows that  $\psi$  is a function of the product  $Ex$  only. Thus, if the variation with  $x$  is known, that with  $E$  can be deduced.

In the actual experiments care is needed, because in order to obtain rays with large energy the pressure in the discharge-tube has to be kept low, and this results in the production of molecular as well as atomic rays. As mentioned above, the proportion of these was measured. Now the molecular rays will probably show more scattering than the atomic. They have twice as many nuclei to be deflected, and for equal energies of the rays, the nuclei in the molecular ray are moving more slowly and so are more easily deflected. Since, however, a collision violent enough to produce a measurable deflexion would almost always result in a dissociation of the molecule, an uncertainty arises, for we have to compare the photographic effect of part of the dissociated molecule with that of the unaffected ray, and there are not sufficient data to enable this to be done.

Fig. 6.



It seems, however, reasonable to suppose that the scattering of a molecule will be a constant multiple of that of an atom, and if we can choose a reasonable number which will reconcile the results of experiments made with varying energies and varying proportions of atoms to molecules, the result is probably correct. I find that if the molecule is taken as 4 times as much scattered as the atoms, the various points lie approximately on a rectangular hyperbola (fig. 6) in agreement with the form found for  $f'(x)$ . In this

curve the scattering in each experiment is found by finding the value of  $k$  which makes  $\frac{k}{\xi} - \frac{k}{\xi + 2a}$  the best fit to the experimentally observed scattering curve and then taking  $k/5$  as the measure of the scattering. The process is equivalent to smoothing the curve and correcting for the finite width of the main beam.

*Comparison with inverse square law of force.*

Although the form of the scattering curve is different from that predicted on the inverse square law, it is of interest to see how the absolute value compares at different parts of the experimental range. In the previous paper the intensity of the scattered rays at a distance  $y$  from the centre of a beam of width  $2a$  and total strength  $I$  was found to be

$$\int_{-a}^a \frac{\pi e^2 N l^3}{6 V^2 (y - \eta)^3} \cdot \frac{I}{2a} \cdot d\eta$$

outside a small distance  $le/Vr$  from the edge of the beam. To compare with our results as reduced above we want the intensity in the limiting case when  $a$  is large, as a fraction of  $I/2a$ . Performing the integration this is

$$\frac{\pi N e^2 l^3}{12 V^2 \xi^2}, \quad \text{where } \xi = y - a \text{ as before.}$$

Here  $V$  is the potential difference through which the rays have fallen to acquire their energy,  $e$  is the charge of an electron,  $N$  is the number of scattering centres of force, and  $l$  is the length of the scattering chamber. In the paper quoted,  $l$  was taken as the distance from the diaphragm corresponding to  $E$  to the plate. Actually some scattering occurs before the diaphragm is reached, and a more accurate investigation shows that one should write  $(l_1^3 - l_2^3)$  for  $l^3$ , where  $l_1$  is the distance from the photographic plate to the centre of the condenser, and  $l_2$  is the distance from the latter to the diaphragm\*. The number of scattering centres per molecule was taken as two, and if the electrons are free to move this is correct, for the maximum angle of deviation would be 1 in 1850 which is too small to be observed. The possibility of an effect of the electrons is considered below.

\* In the previous paper  $l_1$  was 20 cm.,  $l_2$  5 cm.  $(l_1^3 - l_2^3) = 7.875$  against  $(l_1 - l_2)^3 = 3.375$ , thus the calculated scattering as given is too small by a factor of 2.34.

At a pressure of  $\cdot 004$  mm. for rays of 15,000 volts energy scattered through  $\cdot 5$  mm.,

$$\frac{\pi N e^2 (l_1^3 - l_2^3)}{12 V^3 \xi^2}$$

$$= \frac{\pi \cdot 2 \cdot 71 \times 10^{19} \times 2 \times \cdot 004 \times (4 \cdot 77 \times 10^{-10})^3 \times (16^3 - 6^3)}{760 \times 12 \times 50^2 \times (\cdot 05)^2}$$

$$= 1 \cdot 05 \text{ per cent.}$$

The observed value from the curve is 1.86 per cent. The table shows the divergence for other conditions within the range of experiment.

Voltage.	% Scattered through $\cdot 5$ mm.	% Scattered through 2 mm.
5000 { Calc. ....	9.4	1.2
{ Obs. ....	5.6	1.39
15000 { Calc. ....	1.05	.13
{ Obs. ....	1.86	.46
25000 { Calc. ....	.38	.047
{ Obs. ....	1.12	.28

Thus for the slowest rays and small angles the observed scattering is less than that calculated on the simple inverse square hypothesis, while in other cases it is more. The former fact can be explained if it is supposed that the fields of force of the different parts of the molecule partially neutralize one another. It is of interest to consider the distance from the nearest scattering centre at which the rays scattered in various cases will have passed. Owing to the fact that the scattering takes place throughout the volume of the scattering chamber, rays which strike the same portion of the plate will have been scattered through different angles, so that only an average value can be found. Thus take two extreme cases: of the rays of 5000 volts energy 5.6 per cent. are scattered through more than  $\cdot 5$  mm. at  $4/1000$  mm. pressure, while at the same pressure .28 per cent. of the rays of 25,000 volts are scattered through more than 2 mm. Now 5.6 per cent. of the rays pass within  $2 \cdot 0 \times 10^{-9}$  of one of the nuclei, while .28 per cent. pass within  $\cdot 45 \times 10^{-9}$ . These distances then give an idea of the regions in which the observed scattering takes place, assuming that the field of force increases in intensity towards the centres in the molecule. Now take Bohr's model of the molecule to give an idea of dimensions, though it is known not to be accurate. The two nearest centres are at a distance of  $5 \cdot 84 \times 10^{-9}$ . This is about the same as the distance found for the slow rays,

and the defect in scattering in this case may be due to the weak field near the neutral point in the centre of the molecule. This cannot, however, account for the excess of scattering for the faster rays.

It seemed possible that an explanation might be found along the lines that the scattering is not really single, because if the ray comes near one nucleus it has a good chance of being seriously affected by the other. It was found, however, as the result of a somewhat lengthy calculation, that in the case, at least, of the faster rays this effect did not make any appreciable difference to the scattering observed.

The effect of the electrons is difficult to determine, a detailed calculation would involve solving a three body problem, but the following considerations show, I think, that their effect would be small on the classical theory, and probably on the quantum theory also. Since the deflexion due to the free electron is negligible, we shall not be far wrong if we suppose the electron to move so as always to be in a position of equilibrium. But a deflexion such as we have to explain requires an approach to a distance  $\cdot 2 \times 10^{-9}$ , much smaller than any dimension in the molecule. To hold it in equilibrium one of the nuclei must be at a comparable distance on the other side, and it must be very unlikely that the electron would get forced into such a position by the approach of the ray. On the quantum theory it is of course possible that the stationary orbit behaves like something quite rigid, and it might be possible to explain the observed results on these lines; it seems, however, more in accordance with the general ideas of the theory that the electron should move freely if it gets enough energy to move it to the next orbit, and this would give results of the same order as the classical theory.

It must be remembered that the rays used, though charged at the condenser, pick up an electron in a considerable number of cases in the course of their passage through the scattering gas, and it might be supposed that the neutral atom thus formed undergoes greater scattering. This can hardly be the case, however. For suppose the electron given a sudden sideways velocity by collision with a nucleus or otherwise (though not exactly the truth, this will give the order of the effect). The maximum momentum it can transmit to the ray as a whole will be when it is given just sufficient energy to get clear of the attraction of the proton. If  $v$  is the velocity in the orbit this may be changed to  $\sqrt{2}v$  in the opposite direction and the whole change of



momentum  $(1 + \sqrt{2})vm$  transmitted to the nucleus. But the speed of the rays used is not very different from  $v$ , so the angle will be about  $(1 + \sqrt{2})/1850$ , which is too small to detect.

Another argument against the electrons being an important factor is the good agreement between the variation of scattering with the speed of the rays observed and what is deduced from the distribution of scattering in a particular case assuming the scattering particles at rest. Owing to the orbital speed of the electrons being comparable with that of the rays, this would not be likely to hold for electron scattering. Also the shape of the scattering curve is the same for all pressures, while the proportion of neutralized rays increases with the pressure.

It has been shown that the experimental results may be approximately represented by saying that  $f(x)$  varies as  $x^{-2}$ . It is important to deduce from this the collision relation, i. e. the function  $\psi$  such that  $\psi(\theta)d\theta$  is the chance of a particle after collision making an angle between  $\theta$  and  $\theta + \delta\theta$  with its original direction. To do so account must be taken of the fact that the scattering occurs through a volume and that the scattering measured is the component perpendicular to the slits. In the previous paper the inverse square law, for which  $\psi(\theta)$  is proportional to  $\theta^{-3}$ , was shown to lead to the result that the function we have called  $f(x)$  varies as  $x^{-3}$ . It can be shown by a similar argument that if  $\psi(\theta) \propto \theta^{-2}$  then  $f(x) \propto x^{-2}$ , the result obtained experimentally. This then is the form of the collision relation. It can be shown that for small angles of scattering, with which alone we are concerned, a centre of force attracting or repelling as the inverse cube will give a collision relation of this form, but it is not legitimate to deduce that such centres really exist because we cannot be certain that the field of force with which we are concerned is radial round one or more centres in the molecule. It might, for example, be concentrated in the neighbourhood of certain lines of force, in which case the above collision relation, or one like it, might occur with quite a different distribution of the field of force.

There is also the possibility that the whole phenomenon is governed by quantum rather than Newtonian mechanics. It is perhaps worth mentioning that the time integral of the change in kinetic energy of the ray during its passage through the molecule is of the order of Planck's constant.

Further work is in progress on helium and argon and also to investigate the effect mentioned on p. 962 (note).

*Summary.*

A method is described of measuring the scattering of positive rays in a gas by measuring the blackening caused by the impact of the scattered rays on a photographic plate.

The density-exposure curve for positive rays is shown to be similar to that for light.

The angles investigated are of the order of  $\frac{1}{2}^\circ$  and the scattering is shown to be "single."

The results obtained differ widely from what would be expected on the inverse square law, there being an excess of rays scattered through the larger angles. The variation with the speed of the rays is also different from what would be expected.

The collision relation is found to be of the form  $N \propto \theta^{-2} d\theta$ , where  $N$  is the chance of a particle being scattered between  $\theta$  and  $\theta + \delta\theta$  by one encounter.

This relation is what would result from centres of force acting as the inverse cube.

In conclusion I wish to express my sincere thanks to the Department of Scientific and Industrial Research for a grant towards the expenses of an assistant, and to Mr. C. G. Fraser and the assistant in question, Mr. J. D. McKay, for their very able help in the construction and manipulation of the apparatus used in the above work.

Aberdeen.  
Dec. 16, 1925.

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LXXXVIII. *The Fine Structure and Zeeman Effect of Complex Mercury Lines.* By ARTHUR EDWARD RUARK, Associate Physicist\*.

CONTENTS.

- I. Introduction.
- II. Fine Structures of Mercury Lines.
- III. Zeeman Effect of Complex Mercury Lines.
- IV. Zeeman Effect of Complex Cadmium and Thallium Lines.
- V. Conclusion.

I. INTRODUCTION.

**I**N a previous paper † it was shown that the fine structures of spectral lines of non-hydrogenic atoms are due to transitions between the components of complex spectral

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† Ruark & Chenault, *Phil. Mag.* vol. 1, p. 937 (1925). See also Ruark, Mohler & Chenault, 'Nature,' cxiv. p. 575 (1924).

terms. In most cases the complexity of spectral levels is not due to isotopy. Quite frequently complex lines are found in elements which have only a single species of nucleus. Most of the evidence is against the supposition that fine structures are caused by varying orientations of the nucleus (endowed with intrinsic angular momentum) with respect to the electron system of the atom\*, though this interpretation may be right in isolated cases. It is believed that small quantized variations in the orbital configurations of loosely bound electrons suffice to explain the existence of most of the fine structures we have studied.

Frequently it occurs that some of the satellites predicted from the energy diagram of the complex levels fail to appear. This makes it probable that integers called *fine quantum numbers* can be assigned to the components of complex levels, and that there are selection principles to govern the changes of these integers when radiation is emitted.

In the paper referred to, no information was given about the fine structure of mercury lines. This element is richer than any other yet studied in the variety and complexity of its fine structures, which are discussed in Section II. of this paper. Section III. deals with the Zeeman effect of complex mercury lines, while Section IV. discusses the Zeeman patterns of complex lines of other elements. Section V. summarizes the results obtained in III. and IV.

The Paschen notation for spectral terms is used because it is found in practically all the sources of the data which are analysed here.

Only those classifications are given which possess a high degree of probability. An enormous amount of experimental work must be done before this subject reaches its final development, and this paper must be regarded simply as a guide for future research. In the present stage of our knowledge it is impossible to assign fine quantum numbers to the complex levels of Hg in an unambiguous manner.

Since the actual wave-numbers of the satellites are of no importance, we shall follow the usual custom of indicating a satellite by giving its distance  $d\lambda$  from some arbitrary line of the pattern in thousandths of Ångström units, or the corresponding difference in wave-number,  $d\nu$ , in thousandths of  $\text{cm}^{-1}$ . In a few cases it will be necessary to take account of the fact that various authors have used different points of reference in measuring patterns.

\* W. Pauli, Jr., *Naturwissenschaften*, xii. p. 741 (1924). See also Ruark, *Astrophys. J.* lviii. p. 46 (1923).

## II. FINE STRUCTURES OF MERCURY LINES.

Most of the mercury lines whose fine structures have been studied have the final orbits  $2P$ ,  $2p_1$ ,  $2p_2$ , or  $2p_3$ , so there is a wealth of data available for determining the structure of these levels. On the other hand, we cannot hope at present to obtain much knowledge of the higher lying levels. *E. g.*, the level  $4d_3$  is represented only in the line 2652 Å.,  $2p_3-4d_2$ .

It will be convenient to discuss first the lines which end on  $2P$ , and then the important triplet  $2p-2s$ , comprising the lines 5461, 4358, and 4047 Å. After this we shall take up the other lines in the following order:—

4078 Å.,  $2p_2-2S$ .

3663 to 2967 Å.,  $2p-3d$  and  $2p-3D$ .

2652 Å.,  $2p_2-4d_2$ , and 2534 Å.,  $2p_3-4d_3$ .

3341, 2893, and 2752 Å.,  $2p-3s$ .

2925 Å.,  $2p_1-4s$ .

2536 Å.,  $1S-2p_2$ .

The data of Nagaoka, Sugiura, and Mishima\* cover a wider range than those of any other author, and have been used, except where otherwise noted, in the hope that a higher degree of internal consistency might be obtained. Professor J. A. Anderson very kindly sent me some unpublished measurements of the lines 5461, 4358, 4047, 3663·28, 3663·05, 3654, 3650, 5790, 5789, and 5769 Å. These were made from plates obtained by Drs. Anderson and Mackenzie at Johns Hopkins, in the fifth, sixth, and seventh orders of a 96,000-line grating. Allowing for the fact that the origin of measurement are sometimes different, these excellent data are found to be substantially in agreement with those of Nagaoka, Sugiura, and Mishima. It may be said that the patterns of many mercury lines have been definitely ascertained within the limits imposed by variations in the physical condition of the source; for others, the data of various observers are in conflict and further studies are needed.

*Lines Involving the Level 2P.*

The patterns given in Table I. yield considerable information about the structure of the level  $2P$ . The numbers for 5790 Å. are from the grating measurements of Gale and

\* Japanese Journal of Physics, ii. p. 121 (1923).

TABLE I  
Fine Structures of Lines Involving the Level 2P.

5790-66 Å., 2P-3D.				4347-60 Å., 2P-4D.			
$d\lambda$ .	Int.	$d\nu$ .	Classification.	$d\lambda$ .	Int.	$d\nu$ .	Classification.
-188	1	+561					
-121*	4	+361	g-a				
- 78	1	+233	f-a				
- 34	2	+101	e-a				
0	10	0	d-a	0	2	0	d-a
+ 82	1	-245	c-a	+ 47	10	-249	c-a
+131*	3	-391					
+168	1	-502	b-a	+ 97	3	-514	b-a
+227*	3	-678	a-a	+127	3	-672	a-a

5769-60 Å., 2P-3d <sub>2</sub> .				5789-69 Å., 2P-3d <sub>3</sub> .		
$d\lambda$ .	Int.	$d\nu$ .	Classification.	Author.	$d\lambda$ .	$d\nu$ .
-112	2	+337		Gale and Lemon	{ - 67 0	{ +201 0
- 50*	4	+150		Wood .....	{ - 63 0	{ +189 0
0	10	0	g-a	Nagaoka and Takamine ...	{ - 61 0	{ +183 0
+ 44*	5	-132	f-a	Anderson .....	{ -120 - 55 0	{ +360 +165 0
+ 86	1	-258	e-a			
+120	1	-361	d-a			
				Mean of 201, 189, 183, and 165 is 184.		

Lemon\*. For 5789 Å. we record the data of four observers, together with the mean. The values for 5769 Å. represent the mean of several sets of data, all of which are in good agreement. However, Wood† and Nagaoka and Takamine‡ question the existence of the components at -258 and -361. Lunelund§, Gehrccke and von Baeyer, von Baeyer, Janicki, and Nagaoka all give measurements in close agreement with the pattern recorded for 4347 Å.

\* Astrophys. J. xxxi. p. 78 (1910).

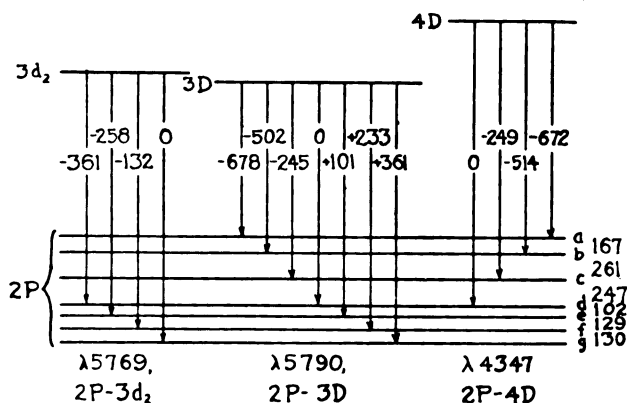
† Phil. Mag. xxv. p. 443 (1913).

‡ Proc. Phys. Soc. London, xxv. p. 1 (1912).

§ Ann. d. Physik, xxxiv. p. 505 (1911). Lunelund gives the complete bibliography.

The similarity of  $2P-3D$  and  $2P-4D$  shows that the differences 247, 261, and 167 arise in the level  $2P$ . The patterns of  $2P-3D$  and  $2P-3d_2$  exhibit the successive mean differences 130, 129, and 102, which therefore belong to  $2P$ . Fig. 1 shows that most of the satellites of these

Fig. 1.


Structures of Lines ending on the Level  $2P$ .

lines can be classified by the use of these differences. The difference 195 in Anderson's data for  $2P-3d_2$  is due to  $3d_2$ . (See the discussion of the lines  $2p-3d$ .) 4344 Å.,  $2P-4d_2$ , is simple according to von Baeyer (*loc. cit.*), while 4339 Å.,  $2P-4d_2$ , was measured as a triplet by Janicki, and as a doublet by Nagaoka. The data will not be given here.

4916 Å.,  $2P-3S$ , is known to be single.

3983 Å.,  $2P-5F$ , was measured by Wendt\*.

This line has a very broad pattern, symmetrical both in spacing and intensity. The intervals of the eight components are

$537 \times 10^{-3} \text{ cm.}^{-1}$   
 366  
 490  
 479  
 477  
 363  
 536

Wendt likewise found coarse patterns for 4078 Å.,  $2p_2-2S$ , and 3341 Å.,  $2p_1-3s$ . While some of the intervals found by

\* *Ann. d. Phys.* xxxvii. p. 535 (1912).

Nagaoka in his study of the last two lines are also represented in Wendt's results, these patterns differ so much from those of other lines that it is probable they have their origin in a physical cause different from that which gives rise to most of the mercury fine structures. For instance, they may be due to the formation of loosely bound  $\text{Hg}_2$  molecules. Without a closer description of the Hg-lamp used by Wendt it would be difficult to say whether the pressure was sufficiently high to justify this view. Lunelund\* studied the Zeeman effect of 5790 Å. and of 5769 Å.

TABLE II.  
Structure of the Lines  $2p-2s$ .

5461 Å., $2p_1-2s$ .				4358 Å., $2p_2-2s$ .			
$d\lambda$ .	Int.	$d\nu$ .	Classification.	$d\lambda$ .	Int.	$d\nu$ .	Classification.
-237	6	+793	c-a	-238	1	+1258	
102	3	341	c-b	206	1	1082	
70	6	234		160	7	844	c-a
47	1.5	157		108	7	566	
19.9	9	66	c-c	95	4	502	b-a
8.4	8	27	a-a	47	1	245	
0	10	0	b-b	21	8	110	c-c
+ 8.2	9	-29		9	8	47	b-b
18.4	8	62		3	10	15	
85	7	285	b-c				
128	3	431	a-b				
214	1	717	a-c				
4047 Å., $2p_3-2s$ .				+ 3	10	15	
$d\lambda$ .	Int.	$d\nu$ .	Classification.	19	5	99	a-a
-116.0	3	+708	c-a	29	3	154	
61.4	9	375	b-a	46	1.5	244	b-c
47.5	5	290		108	7	566	a-b
12.3	9	75		159	3	834	a-c
3.9	9	24	a-a	182	5.5	956	
0	10	0		224	1	1176	
+ 4.1	9	-25	c-c	238	1.5	1251	
59.2	5	361	b-c				
117.0	5	714	a-c				

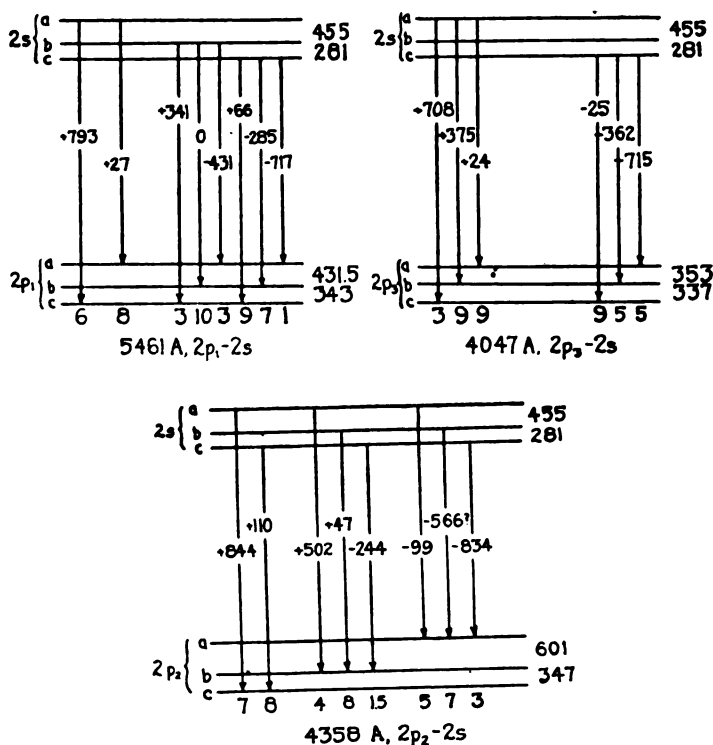
\* *Loc. cit.*

in low fields. The satellites which could be definitely traced are marked with asterisks in Table I. All of these exhibited the same separations as the main lines. (5769 was not fully resolved.) Lunelund observed shifts of the parallel components of some satellites, which throw no light, however, on the problem of classification.

5461, 4358, and 4047 Å.,  $2p-2s$ .

The structures of these lines, as shown in Table II. and fig. 2, are based on a sure foundation of experimental fact.

Fig. 2.



Structures of the Sharp Series Triplet  $2p-2s$ .

They have been studied by a large number of observers, and the results of all those who have done considerable work on fine structures are in substantial agreement. The data given



are those of Nagaoka \*. The existence of numerous unclassified satellites makes it very probable that there are other components of the level  $2s$ . The reader may refer to the section on the lines  $2p-3d$  for information about some doubtful components of the level  $2p_1$ .

4078 Å.,  $2p_2-2S$ .

Five authors agree that the pattern of  $2p_2-2S$  is substantially as given below. The data are those of Nagaoka,

$d\lambda$ .	Int.	$d\nu$ .	Classification.
-77	4	+464	
-47	5	+283	d-a
0	10	0	c-a
+32	3	-193	
+50	5	-361	
+76	2	-457	

Sugiura, and Mishima †. Wendt ‡ observed a complicated pattern nearly one Angström in width, which has not been found by anyone else. (For further details, see the section on lines which involve the level  $2P$ .) He also studied the Zeeman effect of this line in strong fields. Most of the satellites disappear or coalesce, and the pattern becomes a  $3/2$  normal triplet; each of the perpendicular components is accompanied by two satellites, one on either side, at average separations of +192 and -283. There is much evidence that the difference 283 is characteristic of  $2p_2$ .

3663 to 2967 Å.,  $2p-3d$  and  $2p-3D$ .

The data for this group, summarized in Tables III., IV. V. and figs. 3 and 4, are those of Nagaoka, Sugiura, and Mishima, with the following exceptions. The data for 3663.05 show a considerable variation, and those of Wendt have been adopted for the sole reason that they exhibit differences known to be characteristic of  $2p_1$  and of  $3d_1$ . The satellite  $d\nu = +104$  of 3663.28 Å. was observed by Anderson only (unpublished), while the value  $d\nu = -87.3$

\* Proc. Phys. Soc. London, xxix. p. 91 (1917).

† Loc. cit.

‡ Loc. cit.

is the mean of measurements made by Wendt and by Takamine.

TABLE III.

Structures of  $2p_1-3d_{1,2,3}$  and  $2p_1-3D$ .

3663.28 Å., $2p_1-3D$ .				3663.05 Å., $2p_1-3d_2$ .			
$d\lambda$ .	Int.	$d\nu$ .	Classification.	$d\lambda$ .	Int.	$d\nu$ .	Classification.
- 91.0	2	+678		-104	1	+775	c-c
50.7	0.5	378		77	1	574	
14	00	104		26	1	194	a-b
0	10	0	m-a	0	10	0	a-c
+ 9.4	1	- 70	b-a	+ 53	2	-395	
15.9	2	118		109	1/2	813	
32.8	0.2	245					
42.5	0.4	317					
68.1	0.8	508	a-a				
117.0	1	873					

3654.83 Å., $2p_1-3d_2$ .				3650.15 Å., $2p_1-3d_1$ .			
$d\lambda$ .	Int.	$d\nu$ .	Classification.	$d\lambda$ .	Int.	$d\nu$ .	Classification.
-97.3	5	+728		-54.1	4	+406	
72.4	4	542		41.7	5	313	
37.3	1.5	279	c-a	30.1	7	226	n-a
29.8	?	223	n-a	23.9	4	179	
21.3	1	160		16.8	9	126	
7.6	1	57		9.0	2	68	
0	10	0	m-a	0	10	0	m-a
+ 9.5	2	- 71	b-a	+10.3	1	- 77	b-a
33.9	0.5	254		92.4	7	694	
49.3	1	369					
67.7	6	506	a-a				

The patterns of  $3663.28, 2p_1-3D$ ;  $3654, 2p_1-3d_2$ ; and  $3650, 2p_1-3d_1$ , present certain similarities which lead to the introduction of a pair of doubtful components *m* and *n* in the level  $2p_1$ , as shown in fig. 3. The difference 225 appearing in the data for these lines is encountered also in  $2p_1-2s$  and  $2p_1-3s$ .

TABLE IV.

Structures of  $2p_3-3d_{2,3}$ ,  $2p_3-3D$ , and  $2p_3-4d_2$ .

3131.84 Å., $2p_3-3D$ .				3131.56 Å., $2p_3-3d_2$ .			
$d\lambda$ .	Int.	$d\nu$ .	Classification.	$d\lambda$ .	Int.	$d\nu$ .	Classification.
-12.8	1	+130		-82.0	4	+836	
9.9	5	101	d-a?	54.4	1	554	
5.1	1.5	52		23.7	5	242	
0	10	0		13.0	2	133	c-a
+ 5.7	8	- 58		8.3	4	85	
18.0	0.5	184	c-a?	4.3	5	44	
				0	10	0	d-b
				+27.6	5	-282	c-b

3125.66 Å., $2p_3-3d_2$ .				2652.04 Å., $2p_3-4d_2$ .		
$d\lambda$ .	Int.	$d\nu+42$ .	Classification.	$d\lambda$ .	Int.	$d\nu$ .
-205.7	2.5	+2148		-27.9	2	+397
100.8	0.3	1074		15.9	1.5	228
76.8	9	818	d-a	5.5	10	78
48.3	8	537	c-a	0	10	0
35.4	0.5	404		+ 6.3	1	- 90
25.2	2	300		11.3	2	161
14.5	1	190	b-a	22.6	4	322
8.3	4	127		37.5	0.5	534
0	10	42				
+ 12.1	1	- 82				
15.4	0.7	115				
20.2	5	165				
42.1	9	389				
70.6	1	681				

The structure of the lines  $2p_{1,2,3}-3d_3$  shows that the level  $3d_3$  has three components separated by 413 and 195, beginning with the level of smallest wave-number. The difference  $608-413=195$  occurs also in the pattern  $2p_3-4d_3$ , so that  $3d_3$  and  $4d_3$  may have structures which are somewhat similar.

TABLE V.  
Structures of  $2p_3-3d_3$  and  $2p_3-4d_3$ .

2967.28 Å., $2p_3-3d_3$ .				2534 Å., $2p_3-4d_3$ .			
$d\lambda$ .	Int.	$d\nu$ .	Classification.	$d\lambda$ .	Int.	$d\nu$ .	Classification.
-193.8	0.7	+2205		-33.3	6	+518	c-b?
37.9	0.2	431		22.6	7	352	b-a
36.3	8	413	b-a	11.3	9	176	b-b?
29.8	7	339	c-b	0	10	0	a-a
12.7	6	144	c-c	+12.5	5	-195	
5.1	8	58	a-a	24.5	3	389	
0	10	0	b-b				
+ 17.1	3	- 133					

Fig. 3.

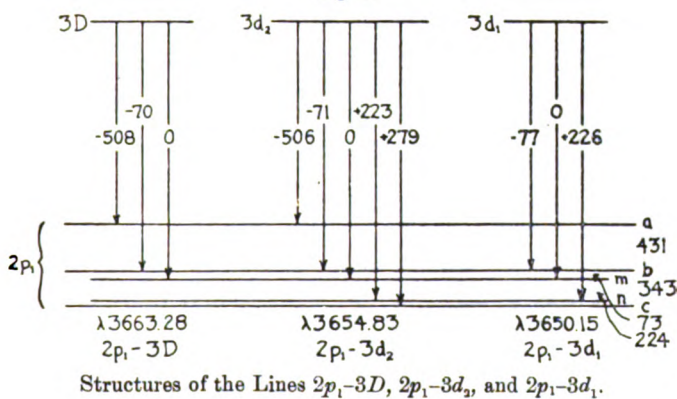


Fig. 4.

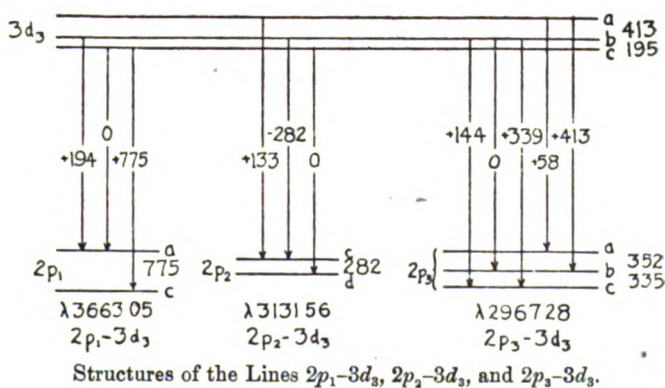


TABLE VI.  
Structures of  $2p_{1,2,3}-3s$  and  $2p_1-4s$ .

3341.48 Å., $2p_1-3s$ .				2893.60 Å., $2p_2-3s$ .			
$d\lambda$ .	Int.	$d\nu$ .	Classification.	$d\lambda$ .	Int.	$d\nu$ .	Classification.
-222.2	0.5	+1990	c-x?	-201.7	2	+2409	
183.8	1.5	1645	b-x?	128.9	0.5	1540	
91.4	2.5	818		68.5	3	818	d-a
79.4	2	711		45.0	0.5	538	c-a
37.3	0.2	334		37.6	0.5	449	
27.0	1.5	242		15.9	0.2	190	b-a
18.8	0.5	168		6.3	6	75	
8.2	8	073		0	10	0	
0	10	0	c-a	+ 8.3	1.5	- 99	
+ 25.1	6	- 225		13.5	0.7	161	
44.0	0.5	394		17.5	3	209	
86.6	5	775	a-a	48.7	1.5	582	
94.8	3	849		68.8	1	822	
137.1	0.3	1228		80.3	1.5	960	
212.2	1	1900					
352.9	4	3160					
400.5	0.1	3588					

2752.78 Å., $2p_3-3s$ .				2925.41 Å., $2p_1-4s$ .			
$d\lambda$ .	Int.	$d\nu$ .	Classification.	$d\lambda$ .	Int.	$d\nu$ .	
-177.3	0.5	+2341		- 69.2	2	+ 809	
121.9	0.5	1610		51.8	1	606	
61.2	1.2	808		20.9	1	244	
25.8	3	341		0	10	0	
21.7	1	287		+ 22.5	2	263	
18.5	0.1	245		69.0	1.5	807	
2.8	9	37		137	0.5	1602	
0	10	0					
+ 28.2	1	- 373	c-a				
53.7	2	710	b-a				
117.0	0.7	1546					
185.5	0.5	2450					
229.5	1	3033					
238.9	0.5	3156					

In the pattern of 3125 Å.,  $2p_2-3d_2$ , we find a group, -165, +190, +537, and +818, which is duplicated in 2893 Å.,  $2p_2-3s$ . The difference 355 between -165 and +190 is not understood, but the other differences involved are easily recognized in other lines ending on  $2p_2$ .

Wendt\* found that 2967·52 Å.,  $2p_2-3D$ , has one satellite at  $d\nu = +704$ . Within the error of measurement, this difference is identical with  $d\nu = 690$ , occurring between the levels a and c of  $2p_3$ .

*Other Lines Involving  $2p_1$ ,  $2p_2$ , and  $2p_3$ .*

None of the satellites of 2652 Å.,  $2p_2-4d_2$ , Table IV., have been classified, but it is worth while to notice that the group -161, -90, 0, and 78 is repeated with great exactitude in the pattern of 2893 Å.,  $2p_2-3s$ .

The data for 2534 Å.,  $2p_3-4d_3$ , Table V., indicate the existence of a difference 176 in  $4d_3$ , but there is no independent check.

The broad and complicated patterns of  $2p_{1,2,3}-3s$ , Table VI., show many resemblances; we record only those classifications which seem reasonably certain. It will be seen that the difference 377 is especially prominent, but it is difficult to interpret.

Professor R. W. Wood has kindly placed at my disposal the results of his investigations on the structure of 2536 Å.,  $1S-2p_2$ . He has shown that many of the components given by Nagaoka, Sugiura, and Mishima are due to self-reversals. The data are given in the table below:—

$d\lambda$ .		$d\nu$ .	Remarks.
Wood.	Nagaoka et al.		
-14	-14·6	+227	
0	0	0	
+10	+ 9·8	-152	{ Nagaoka et al. record lines at +21·6 and 19·3, probably due to self-reversal. The mean is listed here.
+21	+20·4	-318	
+31	+31·5	-490	

Particular attention should be directed to the differences 172 and 166 appearing in this pattern. They are probably characteristic of  $2p_2$ , judging from the frequency with which they occur in other lines involving this level.

\* *Loc. cit.*

*Summary of the Structures of Complex Mercury Levels.*

We give below the differences between the components of complex spectral levels, beginning at the top of the energy diagram.

Energy Level.	$d\nu$ in $10^{-3} \text{ cm}^{-1}$ .	Interval.
$4d_3$ .....	176?	ab
$3s$ .....	1990?	xa
$3d_3$ .....	413	ab
	195	bc
$2s$ .....	455	ab
	281	bc
$2P$ .....	167	ab
	261	bc
	247	cd
	102	de
	129	ef
	130	fg
$2p_1$ .....	431.5	ab
	343	bc
	73?	bm
	224?	mn
$2p_2$ .....	601	ab
	347	bc
	282	cd
$2p_3$ .....	353	ab
	337	bc

## III. THE ZEEMAN EFFECT OF COMPLEX MERCURY LINES.

Nagaoka and Takanine\* have studied the Zeeman effect of 5461, 4359, and 4047 Å. very thoroughly, from the lowest fields which gave an observable splitting up to 30,000 gauss. The reader should refer to their diagrams of the complicated patterns obtained. Unfortunately, they do not give complete tables of numerical data, so the following discussion depends mainly on values obtained from the diagrams.

In commencing the analysis of these patterns, we first note the existence of the following magnetic levels, expressed in terms of the unit  $\Delta\nu_{\text{normal}}$ . These levels behave in approximate accordance with the usual laws, the deviations amounting at most to a few per cent.

\* Proc. Tokyo Math.-Phys. Society, vii. pp. 188 & 331 (1913), or Phil. Mag. xxvii. p. 333 (1914), and xxix. p. 241 (1915).

Line.	Level.		
	a.	b.	c.
2s .....	+2, 0, -2	+2, 0, -2	+2, 0, -2
2p <sub>1</sub> .....	+3/2, 0?	+3, +3/2, 0, -3/2, -3	
2p <sub>2</sub> .....	+3/2, 0, -3/2 *	+3/2, 0, -3/2	+3/2, 0
2p <sub>3</sub> .....	0	0	0

The evidence for these conclusions is drawn from the approximately normal behaviour of certain components of the following satellites :—

Line.	Satellite.	Classification.	Components utilized.
$\lambda$ 5461 .....	0	b-b	
	- 66	a-b	s-component.
	-285	b-c	p-branch of longer wave-length.
	-431	a-b	p-branch.
$\lambda$ 4358 .....	+110	c-c	s-components.
	- 99	a-a	s-components.
	-244	b-c	
	-566	a-b	
$\lambda$ 4047 .....	+ 24	a-a	
	- 25	c-c	
	+375	b-a	s-components.
	-362	b-c	s-components.

Consider the satellites +375 of  $\lambda$ 4047, b-a, and +793 of  $\lambda$ 5461, c-a, which split into two parallel components. The components of shorter wave-length show exactly the same type of separation. It is reasonable to suppose that all the variation is to be ascribed to the magnetic level belonging to "a" of 2s. This shows that "b" of 2p<sub>3</sub> has a level with magnetic quantum number 0, which retains its original position. The same is true of "c" of 2p<sub>1</sub>. It is found that the magnetic level belonging to 2s, a, moves in such a way as to join that level of 2s, b, which has a magnetic quantum number +1. The change is practically complete at 10,000 gauss. This phenomenon is strikingly similar to the Paschen Back effect.

Further analysis of these patterns would be difficult in the present stage of our knowledge. Most of the remaining

\* This value is correct only in weak fields. Separations become greater than  $\pm 3/2$  above 2000 gauss.



components have separations which are not proportional to the field and coalescence of components occur in many cases.

Wendt (*loc. cit.*) has examined the Zeeman effect of the lines  $2p-3d$  and  $2p-3D$  in strong fields. His observations were made with a grating, and it is probable that the details will be somewhat revised when higher resolving powers are applied to the problem. He found that most of the satellites disappear in comparatively weak fields. Wendt gives no numerical data, but states that the patterns of certain lines are in agreement with the findings of Runge and Paschen. The types observed in other cases may be inferred with reasonable certainty from the drawings given. The results are collected in Table VII., where patterns obtained from the drawings are indicated by asterisks.

TABLE VII.

Zeeman Effects of the Mercury Lines  $2p-3d$  and  $2p-3D$ .

$\lambda$ .	Classification.	Observed Zeeman Patterns.	Predicted Zeeman Patterns.	Remarks.
3663.28	$2p_1-3D^*$	?	$\frac{(1, 2, 3, 4)}{2}$	
3663.05	$2p_1-3d_s^*$	$\frac{(2), (4), 1, 5}{2}$	$\frac{(0), (2), 1, 3, 5}{2}$	The interpretation of the observed patterns of 3663.05 and 3654.83 is very doubtful.
3654.83	$2p_1-3d_s^*$	$\frac{(2), (4), (6), 3, 5, 7, 9}{6}$	$\frac{(2), (4), 5, 7, 9, 11}{6}$	
3650.15	$2p_1-3d_1$	As predicted.	$\frac{(0), (1), (2), 6, 7, 8, 9, 10}{6}$	
3131.84	$2p_2-3D^*$	$\frac{(0), (1), 2, 3}{2}$	$\frac{(0), (1), 2, 3}{2}$	There are also $\perp$ components at about $0.6 \Delta\nu$ normal. There are two weak $\perp$ components outside the components $\pm 3/2$ .
3131.56	$2p_2-3d_s^*$	$\frac{(0), (2), 1, 3}{2}$	$\frac{(2), 1, 3}{2}$	
3125.66	$2p_2-3d_2$	As predicted.	$\frac{(0), (2), 5, 7, 9}{6}$	
2967.52	$2p_3-3D$	Normal.	Normal	Satellite at $d\nu = +704$ disappears in strong fields.
2967.28	$2p_3-3d_s$	As predicted.	$\frac{(0), 3}{6}$	

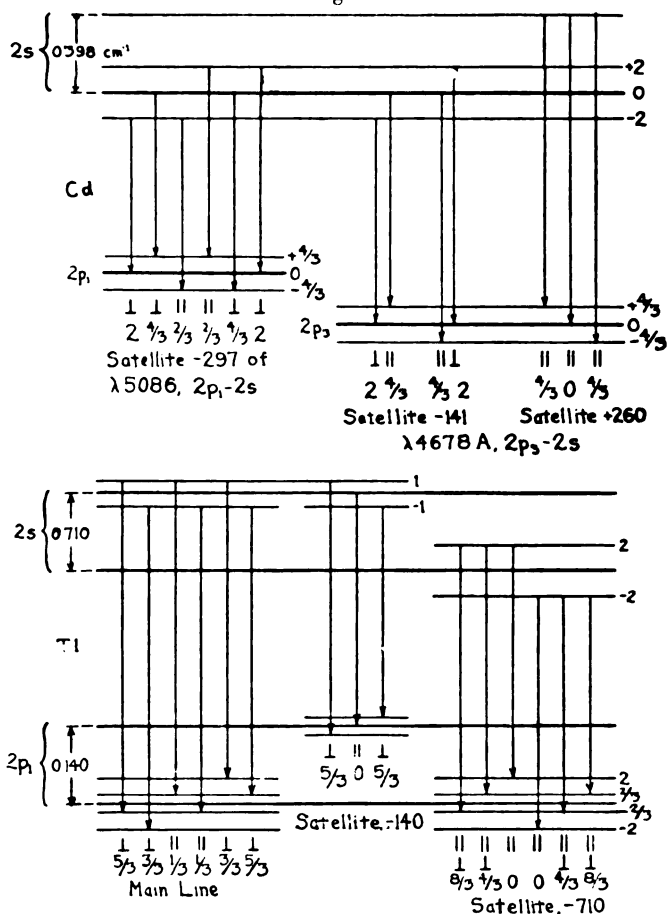
# IV. ZEEMAN EFFECT OF COMPLEX CADMIUM AND THALLIUM LINES.

## 1. Cadmium.

Wali-Mohammad\* studied the Zeeman effect of the cadmium lines  $2p_{1,2,3}-2s$  up to fields of about 5000. The principal lines of these patterns have anomalous Zeeman effects of the usual type.

The more refrangible satellite of 5086 Å.,  $2p_1-2s$ , moves toward the main line; the satellite at  $\Delta\nu = -297$  becomes a

Fig. 5.



Suggested Interpretation of the Zeeman patterns of Complex Cadmium and Thallium Lines.

\* *Ann. d. Phys.* xxxix. p. 225 (1912).

*Phil. Mag. S. 7.* Vol. 1. No. 5. May 1926.

3 S

sextet which may be interpreted as shown in fig. 5. The behaviour of the satellites of 4800 Å.,  $2p_2-2s$ , is so complicated that no certain conclusions can be drawn as to the alterations of the spectral levels. The behaviour of the two satellites of 4678 Å.,  $2p_3-2s$ , is also shown in fig. 5. The satellite at +260 has two perpendicular components at  $\pm 1.60 \Delta\nu_{\text{normal}}$ , which have not been classified. A new satellite appears at +0.018 Å. when the field is applied.

## 2. Thallium.

Back \* found that the main line 2767.913 Å. of the configuration  $2p_2-3d_2$  gives approximately the  $p_2 d_2$  pattern,

$$\frac{\pm (1), 11, 13}{15}.$$

The satellite at  $d\nu = +404$  has a pattern which agrees well with

$$\frac{\pm (1), 25}{15},$$

while the pattern

$$\frac{\pm (1), 11, 25}{15}$$

should be obtained if the  $d_2$  level which is involved in producing this line has magnetic components at  $\pm 2/5$  and  $\pm 10/5$  times  $\Delta\nu_{\text{normal}}$ .

Wali-Mohammad † studied the Zeeman effect of 5350 Å.,  $2p_1-2s$ . The main line has the Zeeman pattern appropriate to its classification,—that is

$$\frac{\pm (1), 3, 5}{3},$$

while the satellite at  $d\nu = -140$  has

$$\frac{\pm (0), 5}{3},$$

and that at  $d\nu = -710$  splits into

$$\frac{\pm (0), (4), (8), 4, 8}{3}.$$

\* *Ann. d. Phys.* lxx. p. 338 (1923).

† *Loc. cit.*

These results can be interpreted as shown in fig. 5. Of course, other arrangements are possible.

## V. CONCLUSIONS CONCERNING THE ZEEMAN EFFECT OF COMPLEX LINES.

The existing observations on the Zeeman effect of complex lines do not suffice to yield us general rules for the prediction of Zeeman patterns from a knowledge of the quantum numbers of a given level.

However, in all patterns which have been investigated definitively the main line has the Zeeman pattern appropriate to simple lines of the same series notation. In general, the "splitting factors" (the  $g$ 's of Landé) are the same for subsidiary components of a complex level as for the corresponding simple levels: for example, many of the mercury satellites show the same type of separation as the main lines. Still, there are exceptions which are experimentally well verified. We have seen that Wali-Mohammad found separations of 2 times  $\Delta\nu_{\text{normal}}$  for the lower component of the level  $2s$  of cadmium, and  $4/3$  times  $\Delta\nu_{\text{normal}}$  for components of  $2p_1$  and  $2p_3$  of that element. These separations are, respectively, characteristic of  $2s$  and  $2p_1$  of a doublet system.

Many cases occur in which expected components are lacking, and anomalies of polarization such as unpolarized components are also found. We have seen many instances in which fine structure separations are unaltered by magnetic fields, just as in hydrogenic atoms, and others in which the components coalesce, so that the  $p$  pattern in strong fields approaches the anomalous Zeeman effect of a simple line of the same classification. W. Pauli, Jr. \*, has pointed out that the latter type of behaviour is to be expected if fine structures are due to varying orientations of a nucleus which possesses an intrinsic angular momentum. Of course, other causes for such a behaviour can readily be suggested.

\* *Naturwissenschaften*, xii. p 741 (1924).

LXXXIX. *Dilatometric Investigation of the  $A_3$  and  $A_4$  Transformations in Pure Iron.* By SEIKICHI SATÔ\*.

§ I. *Introduction.*

THE magnetic investigation of the  $A_3$  and  $A_4$  transformations in iron has already been made by Curie†, Weiss & Föex‡, and others§. Among them Prof. T. Ishiwara, from the result of his experiment with a torsion balance, showed that during heating the magnetic susceptibility of pure iron increases discontinuously at the  $A_4$  point and afterwards gradually decreases, and, on cooling, the change is reversed.

From his study of the  $A_3$  and  $A_4$  transformations with regard to the changes in physical properties of pure iron at high temperatures, Prof. K. Honda predicted that by the  $A_4$  transformation  $\gamma$ -iron will be re-transformed to  $\alpha$ -iron, that is,  $\delta$ -iron will be the same as  $\alpha$ -iron. A year later this was actually confirmed by Westgren|| by X-ray analysis.

The answer to the question, whether during the  $Ac_4$  transformation iron will expand or contract, is not evident; because this depends on the coefficient of expansion of  $\gamma$ -iron. The present investigation was undertaken to decide this point experimentally. Since the  $A_4$  point lies at so high a temperature as  $1400^\circ$ , this investigation is not an easy matter. The writer carried out his investigation with a very pure iron and succeeded in finding a distinct expansion during the  $Ac_4$  transformation. In fact the thermal dilation curve of  $\delta$ -iron formed the continuation of that of  $\alpha$ -iron, showing that the  $\alpha$ - and  $\delta$ -irons are in the same state of aggregation.

§ 2. *Arrangement and Method of Experiment.*

The present experiment was commenced with a dilatometer similar to that used by Prof. K. Honda¶; the heating was effected by the carbon ring electric furnace, devised by Rosenbain and subsequently modified by Lecturer S. Kaya\*\*.

\* Communicated by Prof. K. Honda.

† Curie, *Œuvres*, p. 289.

‡ Weiss & Föex, *Arch. des Sci. Genève*, xxxi. p. 89 (1911).

§ K. Honda & H. Takagi, *Sci. Rep.* iv. p. 261 (1915). T. Ishiwara, *Sci. Rep.* vi. pp. 133-138 (1917). E. M. Terry, *Phys. Rev.* ix. p. 394 (1917).

|| Westgren, *Engineering*, p. 631 (1922); *Stållets Kristallbyggnad* (1921); *Journ. Iron & Steel Inst.* i. p. 240 (1922).

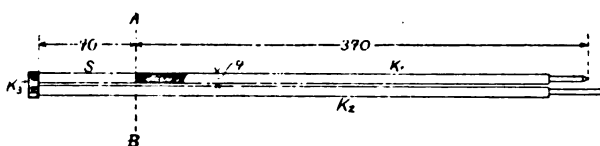
¶ K. Honda, *Sci. Rep.* vi. p. 204 (1917).

\*\* S. Kaya, *Sci. Rep.* (1925-1926).

The furnace worked in a vacuum and gave a sufficient length of uniform heating at very high temperatures, say a maximum variation of only  $2^\circ$  along the length of 70 mm. at  $1300^\circ\text{C}$ . The specimens were cylindrical rods, 6 mm. in diameter and 70 mm. in length, made of armco iron. The linear magnification of the apparatus was 1200, so that at the  $A_3$  point a sharp discontinuous deflexion of scale by about 24 centimetres was observed. But, owing to the yielding of the silica tubes used in the apparatus at very high temperatures, this apparatus could not be used beyond  $1200^\circ\text{C}$ .

After several fruitless trials, a differential method was adopted, a short description of which will be necessary. The specimen and the neutral were connected to form a differential dilatometric couple, as shown in fig. 1. For the neutral metallic cobalt was chosen, because it has no transformation in the vicinity of  $900^\circ$  and  $1400^\circ$ , and its coefficient of expansion, specific heat, and melting-point are of nearly the same values as those of pure iron. In the figure, two rods  $K_1$  and  $K_2$  are cobalt neutrals, having the same diameter as that of specimen  $S$ .  $S$ ,  $K_1$  and  $K_2$ , and a piece of cobalt  $K_3$  are tightly screwed together in the form of a hair-pin,

Fig. 1.



leaving a clearance of about 1 mm. between the two parallel rods. If this pair of connected rods be introduced into the heating furnace so as to heat the left portion of  $AB$  sufficiently uniformly and its left end  $K_2$  be lightly supported, the differential elongation between the iron and cobalt rods will cause a relative displacement between the ends of  $K_1$  and  $K_2$  rods. This displacement can be measured if the right end of  $K_2$  rod be clamped and the same end of  $K_1$  rod be lightly supported and its motion transmitted to a mirror system.

Fig. 2 shows the mirror system. The right end of  $K_2$  rod is clamped to the base  $B$  by a screw  $C$ , and the coned end of  $K_1$  rod touches the end of a quartz tube  $Q$ , which is co-axially fixed to a cylindrical rod  $W$ .  $W$  rests on a horizontal roller  $R_1$  and is guided by two vertical rollers  $R_2$  and  $R_3$ . Hence a displacement of the coned end can be observed as the

deflexion of a small mirror  $M$  attached to  $R_1$ .  $J$  is a screw for adjusting the mirror to the zero position.

Fig. 2.

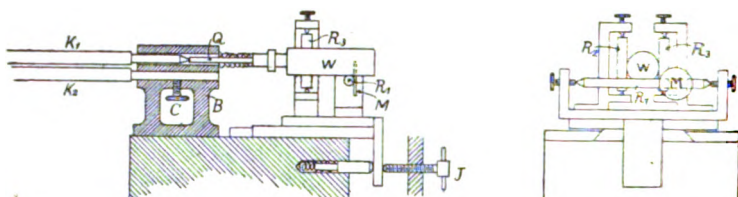
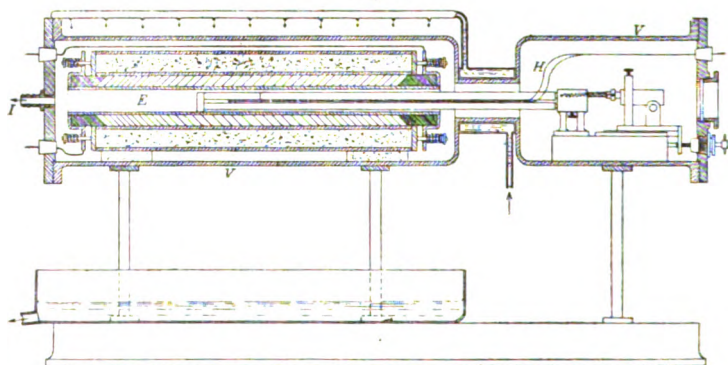


Fig. 3 shows the general arrangement of the apparatus; here the electric furnace, the connected rods, and the mirror system, etc., are put into a closed vessel  $V$ , equipped with a water-cooling device. This vessel is connected with a pump through outlet  $I$ , and the heating and cooling of the specimen can be done in a vacuum. The temperature of the specimen is measured by a Le Chatelier thermocouple  $H$ .  $E$  is the carbon ring electric furnace as stated above.

Fig. 3.



If  $r$  be the radius of the horizontal roller and  $D$  be the scale distance, the relative change of length between the specimen and the neutral, that is,  $\delta l - \delta l_0$ , is given by

$$\delta l - \delta l_0 = r\theta,$$

where  $\theta$  is the deflexion angle of the mirror. Further, if  $n$  be the scale deflexion, we have

$$\tan 2\theta = \frac{n}{D} \div 2\theta,$$

$$\therefore \delta l - \delta l_0 \div \frac{r''}{2D}.$$

In the present case,

$$r=2.50 \text{ mm.}; D=1500 \text{ mm.}$$

$$\delta l - \delta l_0 = \frac{n}{1200} \text{ mm.}$$

The test specimens were cylindrical rods, 7 mm. in diameter and 70 mm. in length. They were made from electrolytic iron melted in a vacuum furnace. The result of the chemical analysis is given below :—

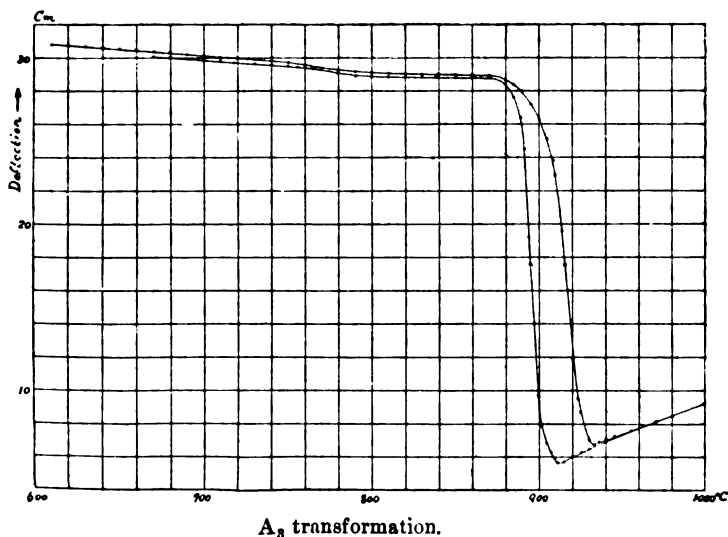
TABLE I.

C (%).	Si (%).	Mn (%).	S (%).	P (%).	Cu (%).
0.006	nil	trace	0.006	nil	nil

### § 3. Results of Experiment.

The change of length during the A<sub>3</sub> transformation was first

Fig. 4.



observed, a typical result of which is given in fig. 4, and in Table II. In the figure, the ordinate represents the scale deflexion and the abscissa the temperature.



TABLE II.

Temperature in deg. C.	Scale Deflexion in cm.	Temperature in deg. C.	Scale Deflexion in cm.
(Heating)		950	7.36
610	30.80	955	7.60
620	30.75	959	7.80
630	30.70	970	8.20
640	30.60	980	8.50
650	30.50	1000	9.20
660	30.45		
670	30.35	(Cooling)	
680	30.30	960	7.75
690	30.20	940	6.90
700	30.15	930	6.50
710	30.05	925	6.30
720	30.00	920	6.00
730	29.87	915	5.70
740	29.81	911	5.62
750	29.76	909	5.90
760	29.59	907	6.30
770	29.40	904	6.80
780	29.24	901	7.80
790	29.15	899	9.70
800	29.10	897	14.00
810	29.04	894	19.20
820	29.01	891	24.50
830	29.00	889	26.40
840	29.00	885	27.60
850	29.00	880	28.40
860	29.00	870	28.80
870	28.94	860	28.80
880	28.69	850	28.80
885	28.40	838	28.80
890	28.00	830	28.80
895	27.20	820	28.80
900	26.30	810	28.80
905	25.10	800	28.80
909	23.80	790	28.85
910	22.90	780	29.06
914	19.60	765	29.36
918	16.00	756	29.40
920	11.90	750	29.41
923	9.50	730	29.60
925	8.70	718	29.70
930	7.00	710	29.80
933	6.70	700	29.83
936	6.95	690	29.90
940	7.10	680	30.00
945	7.23	670	30.05

From fig. 4 we take the scale deflexion due to the  $A_3$  transformation to be

$$n = 240 \text{ mm.}$$

$$\therefore \delta l - \delta l_0 = \frac{240}{1200} = 0.200 \text{ mm.}$$

As the transformation proceeds at a constant temperature, so that

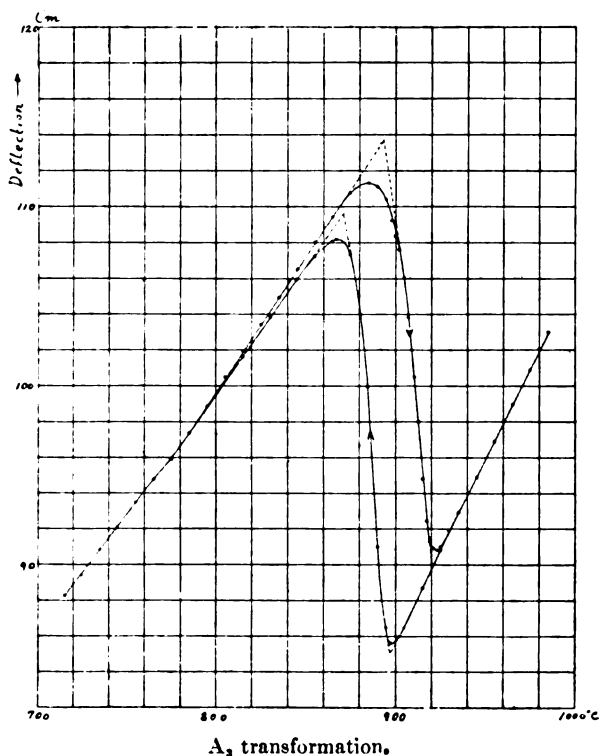
$$\delta l_0 = 0,$$

$$\therefore \delta l = 0.200 \text{ mm.}$$

Next, in order to see the effect of the screwed parts (3.5 mm. thick, 4 mm. long, and  $\frac{1}{32}$  inch pitch) on the value of  $\delta l$ , the following experiment was made :—

Cylindrical specimens of the same length and diameter, *i. e.*,  $70 \times 7$  mm., and of the same material but without the screw ends were prepared, and the change of length due to the  $A_3$  transformation was measured by using the total dilatometer already mentioned. Fig. 5 shows an example of

Fig. 5.



such measurement. Hence we take

$$n = 240 \text{ mm.}$$

$$\therefore \delta l = 0.200 \text{ mm.}$$

*i. e.*, exactly the same result as before. Hence it is to be concluded that the effect of the screwed parts on the change of length is not appreciable.

Let  $l_a$  be the length of the specimen just below the  $A_s$  point and let  $l_\gamma$  be the length of the specimen just above the  $A_s$  point, then we have :—

$$l_a = l_\gamma + \delta l,$$

$$\therefore \frac{l_a}{l_\gamma} = 1 + \frac{\delta l}{l_\gamma},$$

and  $l_\gamma$  can be deduced from the initial length and the scale deflexion at  $920^\circ$  in fig. 5, thus :—

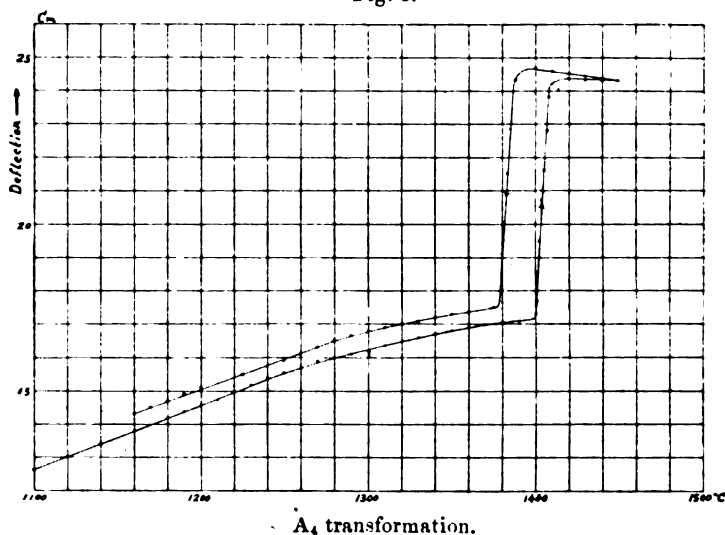
$$n = 900 \text{ mm.}$$

$$\therefore l_\gamma = 70.0 + \frac{900}{1200} = 70.75 \text{ mm.}$$

$$\frac{\delta l}{l_\gamma} = \frac{0.200}{70.75} = 0.00282.$$

Next the heating was further continued to as high as  $1390^\circ \text{C.}$ ; but in this range no abnormal change of length was observed,  $\gamma$ -iron continuously expanding with the rise of temperature, at a rate greater than that of  $\alpha$ -iron. As the temperature reaches  $1400^\circ$  an abrupt increase of length is observed, as shown in fig. 6 and Table III.

Fig. 6.

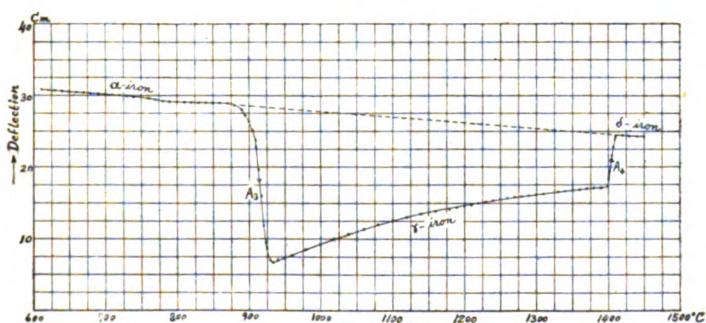


This increase is due to the  $A_4$  transformation. When this discontinuous change has been completed the rate of expansion becomes less than that in the  $\gamma$ -region, and the deflexion-temperature curve lies in the prolongation of that in  $\alpha$ -iron, as shown in fig. 7.

TABLE III.

Temperature in deg. C.	Scale Deflexion in cm.	Temperature in deg. C.	Scale Deflexion in cm.
(Heating)			
1000	9.25	1408	23.80
1020	10.00	1410	24.20
1040	10.70	1420	24.35
1060	11.40	1430	24.30
1080	12.10	1440	24.30
1100	12.60	1450	24.30
1120	13.00	(Cooling)	
1140	13.40	1450	24.30
1160	13.80	1440	24.30
1180	14.20	1430	24.45
1190	14.40	1420	24.50
1200	14.60	1410	24.60
1210	14.71	1400	24.70
1220	15.00	1388	24.30
1230	15.20	1385	22.85
1240	15.40	1383	21.50
1250	15.54	1380	19.10
1260	15.70	1375	17.50
1270	15.90	1360	17.35
1280	16.00	1350	17.30
1290	16.10	1340	17.20
1300	16.20	1330	17.10
1310	16.35	1320	17.00
1320	—	1310	16.90
1330	16.60	1300	16.80
1340	16.70	1290	16.65
1350	16.80	1280	16.50
1360	16.90	1270	16.30
1370	17.00	1260	16.10
1380	17.05	1250	15.90
1390	17.10	1225	15.50
1400	17.30	1200	15.10
1401	17.90	1190	14.90
1402	19.50	1180	14.70
1403	20.70	1170	14.50
1405	21.60	1160	14.30
1407	22.80		

Fig. 7.



This fact confirms the conclusion that  $\delta$ -iron is the same as  $\alpha$ -iron. During cooling, the reversed change takes place at the  $A_{r4}$  point, which lies a little below the  $A_{c4}$  point, i. e., about 20 degrees.

From fig. 6 the scale deflexion during the  $A_4$  transformation is taken to be

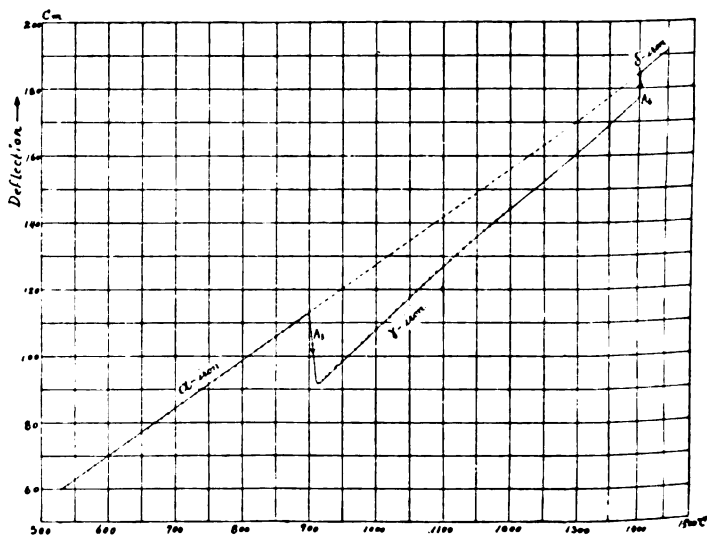
$$n = 73.0 \text{ mm.},$$

and therefore

$$\delta l = \frac{73.0}{1200} = 0.0608 \text{ mm.}$$

Fig. 8 shows an example of the expansion-temperature curve obtained by the total dilatometer. In this case, however, observation beyond  $1200^\circ$  was not possible as stated above; but if the heating curves of both  $\alpha$ - and  $\gamma$ -irons

F



be produced to  $1400^\circ \text{C.}$ , the difference between the ordinates of these curves at this temperature gives an expansion of 73 mm. corresponding to the  $A_4$  transformation which is in satisfactory agreement with the observed value.

If  $l_\gamma$  be the length of specimen just below the  $A_{c4}$  point and  $l_\delta$  be the length of specimen just above the  $A_{c4}$  point, we have

$$l_\delta = l_\gamma + \delta l,$$

$$\therefore \frac{l_\delta}{l_\gamma} = 1 + \frac{\delta l}{l_\gamma}.$$

From the initial length and the scale deflexion given in fig. 8, we obtain

$$l_\gamma = 70.0 + \frac{1770}{1200} = 71.47 \text{ mm.}$$

$$\therefore \frac{\delta l}{l_\gamma} = \frac{0.0608}{71.47} = 0.000851.$$

#### § 4. Comparison of the Results of Experiment with that of X-Ray Analysis.

Let  $a_\alpha$  be the lattice parameter of  $\alpha$ -iron just below the  $A_3$  point, and  $a_\gamma$  be the lattice parameter of  $\gamma$ -iron just above the  $A_3$  point; then one side of an elementary cube occupied by one atom of either  $\alpha$ - or of  $\gamma$ -iron is respectively given by

$$\frac{a_\alpha}{\sqrt[3]{2}} \quad \text{and} \quad \frac{a_\gamma}{\sqrt[3]{4}},$$

and the difference between these two is evidently the contraction or expansion due to the  $A_3$  transformation.

Similarly, if  $a_\delta$  be the lattice parameter of  $\delta$ -iron just above the  $A_4$  point, and  $a_\gamma$  be the lattice parameter of  $\gamma$ -iron just below the  $A_4$  point, then the difference between  $\frac{a_\delta}{\sqrt[3]{2}}$  and  $\frac{a_\gamma}{\sqrt[3]{4}}$  shows the expansion or contraction due to the  $A_4$  transformation.

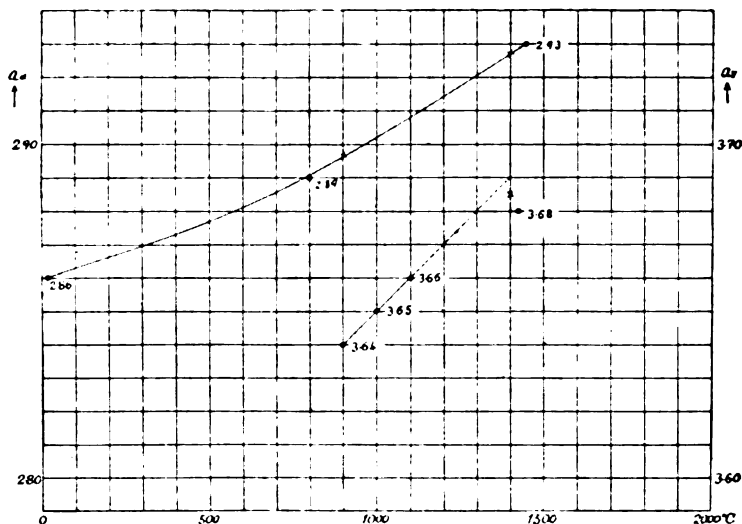
According to Westgren, the values of  $a_\alpha$  and  $a_\gamma$  are as follows:—

TABLE IV.

Temperature.	$a_\alpha(\text{\AA}).$	Temperature.	$a_\gamma(\text{\AA}).$
20° C.	2.86	1000° C.	3.65
800° C.	2.89	1100° C.	3.66
1450° C.	2.93	1425° C.	3.68

The lattice parameters just below and above the  $A_3$  and  $A_4$  points are not given in the table, but they can be found from fig. 9.

Fig. 9.



Thus, at the A<sub>3</sub> point we have

$$a_{\alpha} = 2.897 \text{ \AA} ; a_{\gamma} = 3.640 \text{ \AA},$$

$$1 + \frac{\delta l}{l_{\gamma}} = \frac{2.897}{3.640} \times 1.2599 = 1.00273,$$

or 
$$\frac{\delta l}{l_{\gamma}} = 0.00273,$$

which is in close agreement with the observed value

$$\frac{\delta l}{l_{\gamma}} = 0.00282.$$

Again, at the A<sub>4</sub> point we have

$$a_{\alpha} = 2.927 \text{ \AA}, a_{\gamma} = 3.685 \text{ \AA} ;$$

and hence

$$\frac{\delta l}{l_{\gamma}} = 0.000767,$$

which is also in close agreement with the observed value

$$\frac{\delta l}{l_{\gamma}} = 0.000851.$$

## § 5. Summary.

The present investigation may be summarized as follows:—

(1) In the case of pure iron, during heating, the  $A_4$  transformation is accompanied by an expansion and the  $A_3$  transformation by a contraction, and during cooling these changes are reversed.

(2) The ratio of the magnitudes of the change of length due to the  $A_3$  and  $A_4$  transformations is about 10 : 3.

(3) The thermal dilatation curve of  $\delta$ -iron forms the continuation of that of  $\alpha$ -iron, showing that  $\delta$ -iron is the same as  $\alpha$ -iron.

The writer wishes to express his cordial thanks to Professor K. Honda, under whose kind guidance the present investigation was carried out, and also to Professors T. Ishiwara and M. Yamada for their valuable advice during the course of the present investigation. He is also much indebted to Lecturer S. Kaya for the construction of the electric furnace.

XC. *Germanium in a British Mineral.* By WALTER SCUTT,  
H.M. Inspector, Board of Education\*.

THE occurrence of a noticeable percentage of the very rare element germanium in a British mineral has apparently not been recorded previously. Prof. Hartley, of Dublin, in 1897, writing on "The Wide Dissemination of some of the Rarer Elements" (Journ. Chem. Soc. vol. lxxi. pt. i. p. 533), notes the presence of gallium, indium, and thallium in a variety of British minerals; but he makes no reference to germanium (which had been discovered in 1886 by Winkler in a new silver mineral, Argyrodite, from the Himmelfürst mine near Freiberg, Saxony).

The standard text-books on mineralogy state that germanium is found in appreciable quantities only in the scarce Bolivian minerals Argyrodite ( $4Ag_2S, GeS_2$ ), containing 6–7 per cent. Ge, and Canfieldite ( $4Ag_2S, (SnGe)S_2$ ), containing 1·8 per cent. Ge. To these must now be added Germanite, a sulphide of copper, iron, and germanium, found at Tsumeb in South-West Africa (O. Pufahl, 1922, *Metall und Erz*, Halle, vol. xix. p. 324). This contains about 5–8 per cent. of germanium.

\* Communicated by the Author.



In these three minerals germanium is associated with a large percentage of either silver or copper ; but the position of germanium (atomic number 32) in the Periodic Table would suggest the greater probability of its occurrence in association with zinc (atomic number 30). It therefore seemed to me worth while to make a spectroscopic search for germanium in a number of specimens of zinc blende. The spectrograph used for the purpose is one of my own construction, with a good concave grating of 2 metres radius of curvature, ruled on the Blythswood engine at the National Physical Laboratory, and giving a first-order spectrum which can be photographed on two 12-inch films covering the range from  $\lambda$  7699.3 K to  $\lambda$  2293.9 Cu. This instrument is much simpler in construction than either Rowland's or Eagle's mounting, embodying a plan similar to one of those described by Wadsworth (*Astrophys. Journ.* vol. ii. (1895), p. 370 ; and vol. iii. (1896), p. 46), first suggested to me by Prof. A. Fowler. Both the grating and the photographic film are fixed, and the slit is mounted on a movable radius-arm one metre in length, with a simple automatic arrangement for keeping the plane of the slit at right angles to the line joining the light-source and the centre of the grating.

For producing the spectra, specially pure carbons were cored in the usual way with the powdered minerals, the cored carbon being used as the positive pole of an arc run from the 220-volts D.C. mains through a resistance reducing the current to 2 or 3 amperes.

The spectra of various specimens of blende from Cornwall, Cumberland, and Derbyshire were photographed, and it was found, as one would expect, that the finer, better crystallized, and more attractive the specimen, the less likely was it to contain any of the rarer elements, though cadmium was usually present. On the other hand, some specimens of uninteresting appearance showed traces of one or more of the elements gallium, indium, and thallium (as recorded by Hartley) ; but no trace of germanium was found until a specimen of blende from Wales was examined. This was a dark grey, uncrystallized lump possessing very little lustre, obtained by the writer from an old lead mine in the neighbourhood of Devil's Bridge, Aberystwyth.

Referring to the photograph reproduced, it will be seen that the spectrum of this blende clearly reveals the presence of more than a trace of germanium. The photograph gives the portion of the ultra-violet in which most of the lines of Ge occur, the spectrum of the blende (2) being placed between comparison spectra of zinc (1) and Germanite (3).

Both Germanite and Blende distinctly show the following Ge lines:—3269·5 (between Cd 3261 and Cu 3274); 3039·1 (the least refrangible of a trio, the other two lines being Zn 3036 and Fe 3037·4); 2754·7 (near Zn 2756·5); 2709·7 (near Zn 2712·6); 2691·4; 2651·7/1·3 (seen separate on film with magnifier); and 2592·6.

On comparing the spectrum of Germanite with that of the Blende it will be noted that the relative intensity of the Ge lines in the two spectra is about 2 to 1. Consequently, the exposures having been equal, it is probable that this particular specimen of zinc blende contains from 2 to 4 per cent. of germanium, which is greater than the percentage in Canfieldite. Unfortunately, a direct comparison spectrum of the latter is not given in the photograph, for all my efforts to obtain specimens of Argyrodite and Canfieldite have been fruitless, while the cost of pure germanium metal (£8 5s. a gramme) is prohibitive; but, through the kindness of Dr. Prior, of the Natural History Museum, who informed me of the discovery of Germanite, I was able to get a specimen of this mineral from a London dealer, and this has furnished the interesting comparison seen in the photograph.

London, W. 3.  
February, 1926.

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### XCI. *The Reflexion of X-Rays from Crystals.*

By R. SCHLAPP, *Ph.D.* (Camb.), *University of Edinburgh* \*.

#### 1. *Introduction.*

THE purpose of the following paper is to give an account of the principal phenomena of the X-ray optics of perfect crystals on the basis of the electromagnetic theory of light in continuous media. The method depends on the solution of the equations of propagation of electromagnetic disturbance in a medium whose specific inductive capacity is a periodic function of position. The simplest medium of this type, and the one most amenable to mathematical treatment, is the periodically stratified medium, in which the specific inductive capacity is a periodic function of distance from a given plane. Such a medium appears to suffice for the description of the phenomena under consideration, for the present analysis will be found to reproduce most of the features of propagation and reflexion of X-rays in

\* Communicated by Professor C. G. Darwin, F.R.S.

crystals which have emerged in discussions of the problem by other methods.

The analysis is, of course, applicable without much modification to other instances of selective reflexion due to stratified structure, as, for example, the crystals of chlorate of potash studied by Stokes \* and by Rayleigh †, or the films prepared by Lippmann's process of colour photography ‡. As a typical problem of this class, Rayleigh § investigated the transverse vibrations of a string of periodically distributed density; he was led in this connexion to the differential equation of G. W. Hill, an equation with periodic coefficients, but the solutions which had previously been developed in view of astronomical applications were not well adapted to the physical problem. More recently Hill's equation has been dealt with by methods initiated by E. T. Whittaker, which are peculiarly suited to the present problem, and allow a complete solution to be worked out.

## 2. *The Equations of Propagation.*

The circuital relations of the field may be written

$$-(\dot{\alpha}\dot{\beta}\dot{\gamma}) = \text{curl} (PQR),$$

$$\frac{K}{c^2} (\dot{P}\dot{Q}\dot{R}) = \text{curl} (\alpha\beta\gamma),$$

where  $(PQR)$ ,  $(\alpha\beta\gamma)$  denote the electric and magnetic intensities at a point of the medium at which the specific inductive capacity is  $K$ ,  $c$  the ratio of the electromagnetic to the electrostatic unit of charge, and a dot differentiation with respect to time. The magnetic permeability of the medium is taken as unity. These relations lead to the following equations of propagation of the electric and magnetic intensities :

$$\frac{K}{c^2} (\ddot{P}\ddot{Q}\ddot{R}) = -\text{curl} \text{curl} (PQR),$$

$$\frac{1}{c^2} (\ddot{\alpha}\ddot{\beta}\ddot{\gamma}) = -\text{curl} \frac{1}{K} \text{curl} (\alpha\beta\gamma),$$

together with

$$\text{div}(KP KQ KR) = 0,$$

$$\text{div}(\alpha\beta\gamma) = 0.$$

\* G. G. Stokes, *Proc. Roy. Soc.* xxxviii. p. 174 (1885).

† Rayleigh, *Phil. Mag.* xxvi. p. 256 (1888).

‡ H. E. Ives, *Astrophys. J.* xxvii. p. 325 (1908).

§ Rayleigh, *Papers*, vol. iii. p. 1.

Now suppose that the plane  $y=0$  is taken parallel to the stratifications of the medium, so that  $K$  is a function of  $y$  alone. Then one solution of the propagation equations is given by an electric vector  $(00R)$ , provided  $R$  satisfies

$$\frac{\partial^2 R}{\partial x^2} + \frac{\partial^2 R}{\partial y^2} = \frac{K}{c^2} \frac{\partial^2 R}{\partial t^2},$$

and a second is given by  $(00\gamma)$ , provided  $\gamma$  satisfies

$$\frac{\partial}{\partial x} \frac{1}{K} \frac{\partial \gamma}{\partial x} + \frac{\partial}{\partial y} \frac{1}{K} \frac{\partial \gamma}{\partial y} = \frac{1}{c^2} \frac{\partial^2 \gamma}{\partial t^2}.$$

These two solutions represent fields polarized respectively in and perpendicular to the  $xy$ -plane, which may be taken as the plane of propagation, and accordingly furnish a basis for discussing the propagation of radiation of any state of polarization in the stratified medium.

Assuming  $R$  and  $\gamma$  to be of the form  $R'e^{i(p t - \alpha x)}$  and  $\gamma'e^{i(p t - \alpha x)}$  respectively, we obtain the following equations for  $R'$  and  $\gamma'$ :

$$\frac{d^2 R'}{dy^2} + \left( \frac{p^2}{c^2} K - \alpha^2 \right) R' = 0, \quad \dots \quad (2.1)$$

$$K \frac{d}{dy} \frac{1}{K} \frac{d\gamma'}{dy} + \left( \frac{p^2}{c^2} K - \alpha^2 \right) \gamma' = 0.$$

The second of these may be transformed by the substitution of a new dependent variable  $v$ , given by  $\gamma' = v \sqrt{K}$ . If we suppose the fluctuations of the specific inductive capacity to be small in comparison with its mean value, so that

$$K = K_0(1+h),$$

where  $h$  is so small that its squares and higher powers may be neglected, we find that the equation to be satisfied by  $v$  is

$$\frac{d^2 v}{dy^2} + \left( \frac{p^2}{c^2} K - \alpha^2 + \frac{1}{2} \frac{d^2 h}{dy^2} \right) v = 0. \quad \dots \quad (2.2)$$

In the equations (2.1) and (2.2),  $K$  may be supposed to be expanded in a Fourier's series whose period is  $d$ , the distance between the stratifications

$$\begin{aligned} K = K_0 + K_1 \cos \frac{2\pi y}{d} + K_2 \cos \frac{4\pi y}{d} \dots \\ + K_1' \sin \frac{2\pi y}{d} + K_2' \sin \frac{4\pi y}{d} \dots, \quad \dots \quad (2.3) \end{aligned}$$

where the constants  $K_1, K_2, \dots, K_1', K_2', \dots$ , which determine

the amplitude of the fluctuation of  $K$ , are small in comparison with the mean value  $K_0$  of the specific inductive capacity. All the coefficients of  $K$  will be supposed real; that is, the crystal will be regarded as perfectly transparent. For ordinary crystals and X-ray frequencies  $K_0$  will be very slightly less than unity.

If a new independent variable  $\eta$  be introduced in place of  $\frac{\pi y}{d}$ ,  $R'$  and  $v$  are seen to satisfy an equation which is of the same form in both cases, viz.

$$\frac{d^2 u}{d\eta^2} + [\Psi_0 + 2\Psi_1 \cos(2\eta + \delta_1) + 2\Psi_2 \cos(4\eta + \delta_2) + \dots] u = 0, \quad \dots \quad (2.4)$$

where

$$\Psi_0 = \left(\frac{pd}{\pi c}\right)^2 K_0 - \left(\alpha \frac{d}{\pi}\right)^2,$$

$$\delta_r = -\arctan \frac{K_r'}{K_r},$$

when  $u = R'$  or  $u = v$ , while the coefficients  $\Psi_r$  ( $r \neq 0$ ) are given by

$$\Psi_r = \frac{1}{2} \left(\frac{pd}{\pi c}\right)^2 \sqrt{K_r^2 + K_r'^2}, \quad \text{when } u = R', \quad (2.5)$$

and

$$\Psi_r = \frac{1}{2} \left\{ \left(\frac{pd}{\pi c}\right)^2 - \frac{2r^2}{K_0} \right\} \sqrt{K_r^2 + K_r'^2}, \quad \text{when } u = v. \quad (2.6)$$

Thus in the present problem  $\Psi_1, \Psi_2 \dots$  are constants, while  $\Psi_0$  is a variable parameter depending on  $\alpha$ . It will be seen below how the character of the solution depends on the value of  $\Psi_0$ .

The equation (2.4) resembles the equation introduced in connexion with Lunar Theory by G. W. Hill\*, and commonly known by his name, but it is more general in that all the periodic terms may be affected with phase constants.

### 3. Solution of the Equations of Propagation.

The general theory of differential equations with periodic coefficients shows that a particular solution of the present equation is of the form  $e^{\mu\eta}\phi(\eta)$ , where  $\phi(\eta)$  is a periodic function of period  $2\pi$ , and  $\mu$  and the coefficients of  $\phi$  depend on the constants of the equation. Since the equation is

\* See Whittaker & Watson, 'Modern Analysis,' § 19.12.

unaltered by writing  $-\eta$  for  $\eta$ , and  $-\delta_r$  for  $\delta_r$ , another particular solution is  $e^{-\mu'\eta}\phi'(-\eta)$ , where  $\mu'$  is derived from  $\mu$  and the coefficients of  $\phi'$  from those of  $\phi$  by writing  $-\delta_r$  for  $\delta_r$ . These two solutions may be taken as fundamental solutions, so that the general solution is of the form

$$u = Ae^{\mu\eta}\phi(\eta) + Be^{-\mu'\eta}\phi'(-\eta),$$

where  $A$  and  $B$  are constants.

We shall try to satisfy the equation (2.4), when

$$\Psi_0 = a_0 + a_1\Psi_1 + a_2\Psi_2 \dots,$$

by an expression of the form

$$u = e^{\mu\eta}(1 + b_1\Psi_1 + b_2\Psi_2 + \dots),$$

where  $a_1, a_2 \dots$  are constants, and  $b_1, b_2 \dots$  are periodic functions of  $\eta$ . Terms involving powers of the small quantities  $\Psi_1, \Psi_2 \dots$  higher than the first have not been written down. If we substitute these values of  $u$  and  $\Psi_0$  in the left-hand member of the equation, the coefficients of all powers of  $\Psi_1, \Psi_2 \dots$  must vanish separately. The constant term gives  $a_0 = -\mu^2$ , while that in  $\Psi_r$  gives

$$b_r'' + 2\mu b_r' + a_r + 2\cos(2r\eta + \delta_r) = 0.$$

Since  $b_r$  is to be a periodic function of  $\eta$ ,  $a_r$  must vanish, so that to the present degree of approximation  $\Psi_0 = -\mu^2$  and

$$b_r = \frac{1}{2} \left[ \frac{\cos(2r\eta + \delta_r)}{r^2 + \mu^2} - \frac{\mu \sin(2r\eta + \delta_r)}{r(r^2 + \mu^2)} \right].$$

Hence a particular solution of the equation (2.4) is

$$u = e^{\sqrt{-\Psi_0}\eta} \left[ 1 + \frac{1}{2} \sum \left\{ \frac{\cos(2r\eta + \delta_r)}{r^2 + \mu^2} - \frac{\mu \sin(2r\eta + \delta_r)}{r(r^2 + \mu^2)} \right\} \Psi_r \right].$$

The convergence of this solution breaks down when  $-\mu^2 = r^2$ , that is, when  $\Psi_0$  is near a squared integer; it is, however, valid when  $\Psi_0$  is numerically small. Under these circumstances what may be called the zero-order solution can be written

$$u = e^{\sqrt{-\Psi_0}\eta} \left[ 1 + \frac{1}{2} \sum \frac{\Psi_r \cos(2r\eta + \delta_r)}{r^2 - \Psi_0} \right]. \quad (4.1)$$

Thus for values of  $\Psi_0 \geq 0$  the solution is periodic, while for  $\Psi_0 < 0$  it is affected with a real exponential factor.

The convergence difficulty when  $\Psi_0$  is near a squared integer may be overcome by using the method of solution devised by Whittaker\* in connexion with the equation of

\* E. T. Whittaker, Proc. Edin. Math. Soc. xxxii. p. 75 (1914).

Mathieu, to which the present equation reduces if all the constants vanish except  $\Psi_0$  and  $\Psi_1$ . Whittaker's solution is again of the form  $e^{\mu\eta}\phi(\eta)$ , but, unlike the previous solution, is applicable in the vicinity of  $\Psi_0=r^2$ ; but the way in which  $\mu$  and the coefficients of  $\phi$  depend on the constants  $\Psi_0, \Psi_1, \Psi_2, \dots$  of the equation is so complicated that it is not practicable to express them directly in terms of these constants. The solution depends on the introduction of an intermediate parameter  $\sigma$ ; the quantities  $\Psi_0, \mu$ , and the coefficients of  $\phi$  are then expressible in a conveniently simple form in terms of  $\sigma$  and  $\Psi_1, \Psi_2, \dots$ .

Following Whittaker, we try to determine a solution of the equation (2.4) when  $\Psi_0$  is near a squared integer  $n^2$ , of the form  $e^{\mu\eta}\phi(\eta)$ , where

$$\mu = \kappa_1\Psi_1 + \kappa_2\Psi_2 + \dots,$$

$$\phi = \sin(n\eta - \sigma) + A_1\Psi_1 + A_2\Psi_2 + \dots,$$

$$\Psi_0 = n^2 + \alpha_1\Psi_1 + \alpha_2\Psi_2 + \dots$$

As before, terms of the second or higher order in the small quantities  $\Psi_1, \Psi_2, \dots$  are omitted. The  $\kappa$ 's and  $\alpha$ 's are functions of the parameter  $\sigma$ , and the  $A$ 's are functions of  $\eta$  and  $\sigma$ , which are now to be determined. The parameter  $\sigma$  is not restricted to be real. It will be observed that this solution reduces to the solution

$$u = \sin(n\eta - \sigma)$$

of the corresponding equation

$$\frac{d^2u}{d\eta^2} + n^2u = 0$$

when  $\Psi_1, \Psi_2, \dots = 0$ .

If these expressions be substituted in the differential equation, and successive powers of each of the coefficients  $\Psi_1, \Psi_2, \dots$  equated to zero, certain relations are found, which are sufficient to determine the  $\kappa$ 's,  $A$ 's, and  $\alpha$ 's, if the assumption is made that the functions  $A_1, A_2, \dots$  do not contain terms in  $\cos(n\eta - \sigma)$  or  $\sin(n\eta - \sigma)$ . In this way the terms linear in  $\Psi_r$  give

$$\left. \begin{aligned} \alpha_r &= \kappa_r = 0, \\ A_r &= \frac{\sin\{(n+2r)\eta - \sigma + \delta_r\}}{4r(r+n)} + \frac{\sin\{(n-2r)\eta - \sigma - \delta_r\}}{4r(r-n)} \end{aligned} \right\} (r \neq n),$$

$$\alpha_n = \cos(2\sigma + \delta_n), \quad \kappa_n = \frac{1}{2n} \sin(2\sigma + \delta_n),$$

$$A_n = \frac{\sin(3n\eta - \sigma + \delta_n)}{8n^2}.$$

The solution of the equation (2.4) when

$$\Psi_0 = n^2 + \Psi_n \cos(2\sigma + \delta_n)$$

is accordingly, to the first power of  $\Psi_n$ ,

$$u = e^{\frac{1}{2n} \Psi_n \sin(2\sigma + \delta_n)} \left[ \sin(n\eta - \sigma) + \sum \frac{\sin\{(n+2r)\eta - \sigma + \delta_r\}}{4r(r+n)} \Psi_r \right. \\ \left. + \sum' \frac{\sin\{(n-2r)\eta - \sigma - \delta_r\}}{4r(r-n)} \Psi_r \right], \quad (4.2)$$

where the summations are from  $r=1$  to  $r=\infty$ , and  $\Sigma'$  omits  $r=n$ . This will be referred to as the  $n$ th order solution. We may observe in passing that for a given  $n$ ,  $\Psi_0$  and the exponential factor in  $u$  are determined, within the limits of the present approximation, solely by  $\Psi_n$ .

The form of the solution shows that  $u$  is periodic when  $\sin(2\sigma + \delta_n)$  vanishes; the corresponding critical values of  $\Psi_0$  are  $n^2 \pm \Psi_n$ , which lie in the neighbourhood of the squared integers. We have already seen that  $\Psi_0=0$  is another critical value for which the solution becomes periodic; and examination shows that for values of  $\Psi_0$  between  $-\infty$  and 0, or between the two critical values associated with a squared integer, the index of the exponential factor in the solution is real, while for all other values of  $\Psi_0$ , the index is imaginary.

The two cases correspond respectively to a disturbance decaying or increasing exponentially, and to a periodic disturbance of constant amplitude.

It is, of course, possible to pursue the solution to any desired degree of approximation; but for the physical problem, the present approximation in which squares of  $\Psi_r$  are rejected is sufficiently close.

#### 4. Propagation in the Interior of the Crystal.

The disturbance in the stratified medium is given by a solution of the equation (2.4) multiplied by an exponential factor  $e^{i(pt - az)}$ , subject to  $\Psi_0$  having the appropriate value. The simplest form of propagation in an unlimited stratified medium accordingly consists of a sheaf of plane waves travelling forwards as well as backwards along a discrete series of directions. One of these waves, corresponding to the predominant term in the solution of the generalized Hill's equation, travels with approximately the velocity of light, and is of predominant amplitude; the amplitudes of the waves corresponding to the subsidiary terms of the solution fall off as their direction deviates more from that of



the predominant wave, and their velocities likewise diverge from the normal value, those on one side travelling faster and those on the other side slower. Thus the phase velocity of part of the disturbance is greater than the velocity of light in *vacuo*; such a velocity is admissible, as it applies to the phase of a permanent state of propagation, and not to a disturbance seeking fresh ground.

For certain directions of propagation the interior disturbance is affected with an exponential damping factor causing decay to  $1/e$  after penetrating a distance

$$\frac{2nd}{\pi\Psi_n \sin(2\sigma + \delta_n)};$$

this distance attains its minimum value  $\frac{2nd}{\pi\Psi_n}$  when

$$2\sigma + \delta_n = \frac{\pi}{2},$$

that is, when  $\Psi_0 = n^2$ . The damping factor clearly represents the effect of partial reflexions from the successive strata in robbing the primary beam, incident at the proper angle, of its energy, while the reflected beam is correspondingly enhanced. The transfer of energy between the two beams is effected, as Darwin showed, by the multiple reflexions which take place between the strata, in the sense that portions of the primary beam which have suffered an even number of reflexions are travelling in the same direction as the primary beam, but have a retardation of an odd number of half wave-lengths on it, and interfere destructively with it; the energy so destroyed reappears, completely in the absence of ordinary absorption, in the reflected beam. Darwin's primary extinction is accordingly represented in the present analysis by the exponential factor affecting the solution of the generalized Hill's equation.

### 5. Reflexion from the Face of a Stratified Medium of Infinite Depth.

Suppose the medium to occupy all space on the negative side of the plane  $y=0$ , so that the face is parallel to the stratifications. Let plane waves, polarized in the plane of incidence, fall on the face in a given direction. The electric intensity  $R_1$  outside the medium may then be written, apart from a factor  $e^{i(pt - \alpha x)}$ ,

$$R_1 = Ae^{im\eta} + Be^{-im\eta}, \quad . \quad . \quad . \quad (51)$$

where A and B are constants, in general complex, giving

amplitude and phase of the incident and reflected waves, and  $m$  determines the glancing angle  $\theta$  of incidence or reflexion in accordance with the equation

$$\sin \theta = m \frac{\pi c}{pd}.$$

Inside the medium the electric intensity is represented by one of the fundamental solutions of equation (2.4), that solution being chosen which gives a disturbance decaying as it penetrates the medium. This solution is determined by the value of  $\Psi_0$ , which in turn depends on  $m$ , and therefore on  $\theta$ . Since the disturbance is propagated with velocity  $c$  outside the medium,

$$\begin{aligned} m^2 &= \left(\frac{pd}{\pi c}\right)^2 - \left(\alpha \frac{d}{\pi}\right)^2 \\ &= \left(\frac{pd}{\pi c}\right)^2 (1 - K_0) + \Psi_0, \quad \dots \quad (5.2) \end{aligned}$$

so that

$$\sin^2 \theta = 1 - K_0 + \left(\frac{\pi c}{pd}\right)^2 \Psi_0. \quad \dots \quad (5.3)$$

Thus for real angles of incidence,  $\Psi_0$  must be greater than  $-\left(\frac{pd}{\pi c}\right)^2 (1 - K_0)$ , so that we may confine our attention to the zero-order solution (4.1) of equation (2.4), which is valid when  $\Psi_0$  is numerically small, and to the solutions (4.2), valid when  $\Psi_0$  has values near the squared integers.

For small values of the glancing angle  $\theta$ , corresponding to small values of  $\Psi_0$ , we may write for the electric intensity inside the medium

$$R_2 = D e^{\sqrt{-\Psi_0} \eta} \left[ 1 + \frac{1}{2} \sum \frac{\Psi_r}{r^2 - \Psi_0} \cos(2r\eta + \delta_r) \right], \quad (5.4)$$

where  $D$  is a complex constant, and a factor  $e^{i(pt - ax)}$  has been omitted as before. The solutions (5.1) and (5.4) are now to be fitted together in accordance with the usual

boundary conditions of continuity of  $R$  and its gradient  $\frac{\partial R}{\partial \eta}$  across the interface  $y=0$ . These conditions give

$$A + B = Du,$$

$$im(A - B) = D[u \sqrt{-\Psi_0} - v],$$

where

$$u = 1 + \frac{1}{2} \sum \frac{\Psi_r \cos \delta_r}{r^2 - \Psi_0},$$

$$v = \sum \frac{r \Psi_r}{r^2 - \Psi_0} \sin \delta_r.$$

On eliminating  $D$ , we obtain

$$\frac{B}{A} = \frac{i\beta - 1}{i\beta + 1}, \quad \dots \dots \dots (5.5)$$

where

$$\beta = \frac{mu}{u \sqrt{-\Psi_0 - v}}.$$

For larger glancing angles, corresponding to

$$\Psi_0 = n^2 + \Psi_n \cos(2\sigma + \delta_n),$$

the interior disturbance is

$$R_2 = D e^{\frac{1}{2n} \Psi_n \sin(2\sigma + \delta_n) \cdot \eta} [\sin(n\eta - \sigma) + \dots],$$

and the equations of continuity at the interface are, to a sufficient approximation,

$$A + B = -D \sin \sigma,$$

$$im(A - B) = Dn \cos \sigma,$$

whence

$$\frac{B}{A} = -e^{2i \arctan \frac{m}{n} \tan \sigma} \dots \dots (5.6)$$

The interpretation of the symbolic expressions (5.5) and (5.6) for the ratio of the amplitudes of the reflected and incident waves readily follows. Taking the expression (5.5), we see that  $\beta$  is real so long as  $\Psi_0$  is negative, or, since  $m^2$  is essentially positive, so long as  $m^2$  lies between 0 and  $\left(\frac{pd}{\pi c}\right)^2 (1 - K_0)$ . This range of values of  $m$  for which  $\beta$  is real corresponds to glancing angles of incidence between 0 and  $\arcsin \sqrt{1 - K_0}$ ; in it the modulus of  $\frac{B}{A}$  is unity, so that the reflexion is perfect. Angles of incidence immediately outside this range correspond to small positive values of  $\Psi_0$ , so that  $\beta$  takes complex values; examination shows that the modulus of  $\frac{B}{A}$  rapidly falls towards zero outside the range of perfect reflexion.

In the expression (5.6) we may, by (5.2), write  $n$  for  $m$  so long as  $\Psi_0$  is near a squared integer  $n^2$ . The ratio of the reflected to the incident amplitude is therefore approximately  $-e^{2i\sigma}$ , the modulus of which is unity so long as  $\sigma$  is

real. Let  $\phi$  be the glancing angle corresponding to

$$\sigma = \frac{\pi}{4} - \frac{\delta_n}{2},$$

so that from (5.3)

$$\sin^2 \phi = 1 - K_0 + n^2 \left( \frac{pd}{\pi c} \right)^2 \quad . \quad . \quad . \quad (5.7)$$

In the neighbourhood of  $\phi$  let  $\theta = \phi + \epsilon$ , where  $\epsilon$  is small. Then (5.3) and (5.7) give

$$\epsilon = \frac{\Psi_n \lambda}{4nd \cos \phi} \cos (2\sigma + \delta_n).$$

We see, then, that so long as  $\sigma$  is real,  $\theta$  is restricted to the range

$$\phi \pm \frac{\Psi_n \lambda}{4nd \cos \phi},$$

and that within this range the reflexion is perfect, but accompanied by a phase change.

For glancing angles outside this range  $\cos (2\sigma + \delta_n)$  must be real and numerically greater than unity, so that  $\sigma$  is of the form

$$is - \frac{\delta_n}{2} \quad \text{or} \quad \frac{\pi}{2} + is - \frac{\delta_n}{2},$$

where  $s$  is real. The amplitude of reflexion has then the modulus  $e^{-2s}$ , which falls off very rapidly outside the range of perfect reflexion; at a distance from the edge equal to about half the width of the band the amplitude of reflexion has fallen to about 27 per cent. of totality. The amplitude of reflexion  $e^{-2s}$  may readily be expressed in terms of glancing angle  $\phi + \epsilon$ . If  $\epsilon_1$  denote the half-width of the range of perfect reflexion, the values of the amplitude appropriate to the three regions

$$\epsilon < -\epsilon_1, \quad -\epsilon_1 < \epsilon < \epsilon_1, \quad \epsilon > \epsilon_1$$

are respectively

$$-\frac{\epsilon + \sqrt{\epsilon^2 - \epsilon_1^2}}{\epsilon_1}, \quad 1, \quad \frac{\epsilon - \sqrt{\epsilon^2 - \epsilon_1^2}}{\epsilon_1}.$$

These are equivalent to the formulæ given by Darwin\*.

The reflexion from the crystal is therefore negligible except over certain ranges of angles of incidence, in which there is perfect reflexion, and in the regions immediately

\* C. G. Darwin, Phil. Mag. xxvii. p. 675 (1914).

bordering these ranges, in which the reflexion rapidly falls off to zero. The ranges of perfect reflexion are from 0 to  $\arcsin \sqrt{1-K_0}$ , and ranges of width  $\frac{\Psi_n \lambda}{2nd \cos \phi}$  symmetrical about positions  $\phi$  given by (5.7). The first of these regions may be regarded as arising by the total reflexion of the X-rays at the crystal face, while the others are the reflexions at the Bragg angles of spectra of the 1st, 2nd, ...  $n$ th order.

The value  $\arcsin \sqrt{1-K_0}$  of the critical glancing angle shows that the crystal behaves, as regards total reflexion, like a homogeneous optical medium of refractive index  $\sqrt{K_0}$ . It will be observed that the  $n$ th order band of reflexion is symmetrical about a position given by (5.7), which differs slightly from the position

$$\phi_0 = \arcsin n \frac{\pi e}{pd}$$

given by Bragg's relation. If we denote  $1-K_0$  by  $2t$ , we find

$$\phi - \phi_0 = t \sec \phi \operatorname{cosec} \phi,$$

which is the relation obtained by Darwin\* on the assumption that Bragg's formula holds accurately within the crystal, but that owing to a refractive index less than unity by  $t$ , corresponding to a mean specific inductive capacity  $1-2t$ , the angle  $\phi$  of incidence on the face of the medium is not the same as the angle of passage across the stratifications.

The range of perfect reflexion is in each case bordered by a region in which the reflexion falls off. Calculation shows that the region of perfect reflexion contributes to the area under the curve of intensity against glancing angle a constant fraction, equal to three quarters, of the whole.

Numerical estimates may be obtained by writing for the specific inductive capacity the Drude-Lorentz expression

$$K = 1 - \frac{\rho e^2}{\pi m \nu^2},$$

where  $\nu$  is the frequency ( $= \frac{p}{2\pi}$ ), and  $\rho$  the density of distribution of electrons. If  $\rho$  be expanded in a Fourier's series

$$\begin{aligned} \rho = \rho_0 + \rho_1 \cos 2\eta + \rho_2 \cos 4\eta \dots \\ + \rho_1' \sin 2\eta + \rho_2' \sin 4\eta \dots, \end{aligned}$$

\* C. G. Darwin, *Phil. Mag.* xxvii. p. 315 (1914).

comparison with (2.3) gives the values

$$K_0 = 1 - \frac{4\pi e^2 c^2}{mp^2} \rho_0,$$

$$K_r = -\frac{4\pi e^2 c^2}{mp^2} \rho_r, \quad K_r' = -\frac{4\pi e^2 c^2}{mp^2} \rho_r'.$$

For illustrative purposes we may take a medium in which the stratification of electron density is represented by only two terms of the series, so that

$$\rho = \rho_0 + \rho_1 \cos 2\eta.$$

Since  $\rho$  vanishes midway between the planes of greatest concentration,  $\rho_1 = \rho_0 =$  mean density of electrons in the crystal. If we use as typical values

$$d = 2.81 \times 10^{-8}, \quad \frac{e}{m} = 5.3 \times 10^{17},$$

$$\rho_1 = 6.3 \times 10^{23}, \quad e = 4.77 \times 10^{-10},$$

$$c = 3 \times 10^{10},$$

we find that  $\Psi_1$  is of the order of magnitude  $10^{-5}$ , which justifies the rejection of  $\Psi_1^2$  in comparison with  $\Psi_1$ . The breadth of the range of perfect reflexion in the first order of the platinum  $\beta$  radiation ( $\lambda = 1.11 \times 10^{-8}$  cm.) is about 3.7 seconds of arc, and at the centre of the range the radiation is damped to  $\frac{1}{e}$  after traversing about 6000 atomic planes.

## 6. Intensity of Reflexion from a Deep Crystal.

### *The Polarization, Structure, and Temperature Factors.*

The widths of the reflexion ranges in the various orders are much too small to be directly observable, and in any actual experiment the finite size of the source and of the crystal would give rise to a complicated diffraction pattern. The intensity of reflexion of homogeneous radiation in any order, or "integrated reflexion" as usually observed, will, however, be proportional to the width of the range of perfect reflexion. Thus any cause which affects the intensity of reflexion must operate by altering this width, or, since the width in the  $n$ th order is proportional to  $\Psi_n$ , by altering  $\Psi_n$ .

The conclusion that the reflexion in any order is proportional to the corresponding harmonic term in the Fourier's series for the stratified reflecting power, which is equivalent to the present result, and which has an analogue in the theory

of the plane optical diffraction grating, was arrived at by Bragg\*, whose investigation does not, however, exhibit the dependence of the reflexion on the width of the range over which it is perfect. In terms of the present analysis, the result rests on the peculiarity of the differential equation of the problem which was pointed out above, namely that its  $n$ th-order solution is determined chiefly by the  $n$ th-order coefficients in the expansion of  $K$ .

We may see in a general way how the width of the range of reflexion is governed by the fluctuation about a mean value of the specific inductive capacity, or, what comes to the same thing, by the reflecting power of the crystal planes, by using the principle that the resolving power of a diffracting system—that is, the narrowness of the range over which homogeneous radiation is reflected—is proportional to the number of diffracting elements. Since the radiation is rapidly damped in its passage through the medium at the proper angle by the operation of extinction, the deeper-lying strata are inoperative in determining the purity of the spectrum. The smaller the reflecting power of each layer, the greater will be the number of layers contributing to the whole reflexion, and the narrower the corresponding range of reflexion.

For radiation polarized perpendicular to the plane of incidence, the quantity  $v = \gamma' / \sqrt{K}$ , where  $\gamma'$  is that part of the magnetic vector independent of  $t$  and  $x$ , was seen to satisfy the same equation (2.4) as  $R'$ , except that  $\Psi_n$  is now given by (2.6) instead of (2.5). An investigation similar to that of the preceding paragraph shows that the reflexion of  $v$ , and therefore of  $\gamma$ , is perfect over a range whose width is proportional to the new value of  $\Psi_n$ , and which is accordingly

$$1 - \frac{2n^2}{K_0} \left( \frac{\pi c}{pd} \right)^2 \text{ times the width of the range of perfect}$$

reflexion of  $R$ . Thus the intensity of reflexion of the constituent of unpolarized radiation which is polarized perpendicular to the plane of incidence differs from the intensity of reflexion of the constituent polarized in the plane of incidence by the factor

$$\left| 1 - \frac{2n^2}{K_0} \left( \frac{\pi c}{pd} \right)^2 \right|,$$

which may be written, since

$$\frac{n^2}{K_0} \left( \frac{\pi c}{pd} \right)^2 \doteq \sin^2 \phi,$$

\* W. H. Bragg, Phil. Trans. ccxv. A, p. 268 (1915).

as  $|\cos 2\phi|$ . The intensity of reflexion of unpolarized radiation is accordingly obtained from the expression for the intensity of reflexion of radiation polarized in the plane of incidence by multiplication by a factor

$$\frac{1}{2}(1 + |\cos 2\phi|).$$

The structure factor expresses the reflexion from a crystal face the planes parallel to which are of two or more distinct types, alternating regularly, in terms of the reflexion from ideal crystals in which the planes are all of one type.

For simplicity we suppose that the variable part of the distribution of specific inductive capacity, or of negative electron density, may be regarded as the superposition of two parts, each of which is due to a different kind of atomic plane, and each of which is taken to be symmetrical, and expressed by

$$\begin{aligned} & -\rho_1 \cos 2\eta - \rho_2 \cos 4\eta \dots \\ \text{and} \quad & -\rho_1' \cos 2(\eta - \delta) - \rho_2' \cos 4(\eta - \delta) \dots, \end{aligned}$$

so that  $\frac{d\delta}{\pi}$  is the displacement of the one set of planes relative to the other. The variable part of the resultant specific inductive capacity throughout the crystal will be proportional to the sum of these two parts, that is, to

$$\Sigma(\rho_r + \rho_r' \cos 2r\delta) \cos 2r\eta + \Sigma\rho_r' \sin 2r\delta \sin 2r\eta,$$

and the intensity of reflexion will accordingly contain a factor

$$\begin{aligned} & [(\rho_r + \rho_r' \cos 2r\delta)^2 + (\rho_r' \sin 2r\delta)^2]^{\frac{1}{2}} \\ & = [\rho_r^2 + \rho_r'^2 + 2\rho_r\rho_r' \cos 2r\delta]^{\frac{1}{2}}. \end{aligned}$$

If we assume that the shapes of the two constituent distributions are the same, that is, that  $\frac{\rho_r'}{\rho_r}$  is independent of  $r$  and equal to the ratio  $\frac{Z'}{Z}$  of the mean densities in the two types of planes, we obtain for the structure factor the usual expression

$$[Z^2 + Z'^2 + 2ZZ' \cos 2r\delta]^{\frac{1}{2}}.$$

As a rough approximation it may be said that the effect of temperature is to cause the atoms to execute oscillations about their mean positions, and that the departures of their centres from the median plane at any instant follow the



usual distribution law; on this assumption a factor representing the influence of temperature vibrations on the intensity of reflexion may readily be deduced. Suppose that at the absolute zero the electron density corresponding to a series of atomic planes may be written as a cosine series

$$\rho_0 + \rho_1 \cos 2 \frac{\pi y}{d} + \rho_2 \cos 4 \frac{\pi y}{d} \dots$$

When displaced a distance  $y'$  from the equilibrium position in a direction perpendicular to the plane, the atom giving rise to this distribution contributes to the electron density at  $y=Y$  an amount

$$\rho_0 + \rho_1 \cos \frac{2\pi}{d} (y' - Y) + \rho_2 \cos \frac{4\pi}{d} (y' - Y) \dots$$

Now the relative number of atoms in any plane displaced through distances between  $y'$  and  $y' + dy'$  is

$$\sqrt{\frac{\sigma}{2\pi kT}} e^{-\frac{1}{2} \frac{\sigma y'^2}{kT}} dy',$$

where  $\frac{1}{2}\sigma$  is the potential energy for unit displacement,  $T$  the absolute temperature, and  $k$  is Boltzmann's constant, so that the density at  $y=Y$  is

$$\begin{aligned} \int_{-\infty}^{\infty} \sqrt{\frac{\sigma}{2\pi kT}} \left( \rho_0 + \rho_1 \cos \frac{2\pi}{d} (y' - Y) \dots \right) e^{-\frac{1}{2} \frac{\sigma y'^2}{kT}} dy' \\ = \rho_0 + \sum \rho_r e^{-\frac{2kT}{\sigma} \frac{r^2 \pi^2}{d^2}} \cos \frac{2r\pi Y}{d}. \end{aligned}$$

Hence the intensity of reflexion in the  $n$ th order is affected with the factor

$$e^{-\frac{2kT}{\sigma} \frac{n^2 \pi^2}{d^2}},$$

which is of the usual exponential form. But the assumptions on which this calculation is based are not refined enough for a comparison of the result with experiment.

The above analysis leads to values of the factors representing the influence on the intensity of reflexion of polarization, structure, and temperature, which are the square roots of the values obtained by a simpler theory in which each plane is assumed to scatter independently of the others. This result is in general agreement with Darwin's

later results, and with the more recent investigations of Ewald\*.

In view of the short wave-length of X-rays, in comparison with which ordinary matter must be regarded as coarse-grained, it is remarkable that the crystal should be capable of being treated as a continuous optical medium. A suggested explanation is that when the radiation traverses the crystal in a direction near the reflecting angle, the portions of the incident wave-train which contribute to any wave-front of the reflected train are spaced out at intervals  $2d \sin \theta = n\lambda$  behind each other, and therefore meet successive planes in the same phase, so that each reflected wave-front is made up of contributions coming from all the planes. This makes it possible to average out the irregularities of the individual planes over their whole number, or, in other words, to replace the discrete electronic structure of each plane by a continuous distribution.

I wish to express my indebtedness to Sir Joseph Larmor, at whose suggestion this investigation was undertaken.

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December 1925.

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XCVII. *On the Influence of Radiation on Ionization Equilibrium.*  
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1.

THE chief desideratum of the present theories of thermal ionization of gases is that they fail to take any account of the influence of radiation on ionization equilibrium. Yet it can easily be shown, and it has been pointed out by many investigators, that radiation plays an essential rôle in many physical and astrophysical phenomena. Russell‡ pointed out the possible influence of radiation in the barium-sodium anomaly in the solar photosphere, where barium is found to be almost completely ionized, while sodium is only partially ionized, though both elements possess identical ionization potentials. He traced the phenomena to the fact that

\* P. P. Ewald, *Phys. Ztschr.* xxvi. p. 29 (1924).

† Communicated by the Authors.

‡ Russell, *Astrophysical Journal*, lvi. May 1922.

$Ba^+$ -atoms are susceptible to photospheric radiation, because the resonance lines lie at 4934, 4554, while  $Na^+$ -atoms are not so, because their resonance lines probably lie far in the ultra-violet. Milne\* points out that radiation pouring out through the solar atmosphere is at a higher temperature than the atmosphere itself, and hence the observed ionization is at least partly due to radiation. In recent years, experiments† have been done in which comparatively cool vapours of alkalis have been ionized by ultra-violet radiation lying beyond the convergence frequency of the principal series of the element. In such cases, the ionization is a purely radiation effect. To the same class of phenomena belong the familiar absorption experiments of Wood and others, where vapours of metals are illuminated by continuous light. In this case the atoms are not ionized, but as a result of the interaction between matter and radiation the valency electron is lifted to higher orbits. There is, in fact, no essential difference between this class of phenomena and phenomena known as photo-chemical reactions, only in the latter case the unit mechanism of reaction is rather obscure.

The treatment of this class of phenomena from the theoretical side is fraught with several difficulties, viz. (1) the mechanism of absorption of a pulse of light by an atom has not yet been tackled successfully on the quantum-mechanical basis; (2) in a reaction of this type, the reacting pulses do not all have the same frequency, i. e. the absorption lines have a finite breadth. This means that when pulses slightly differing from the resonance lines collide with the atom, there is a probability of their being absorbed, but the value of this probability factor varies from a maximum for the centre of the absorption line to rapidly decreasing values on both sides of the centre. Again, the maximum absorption varies from line to line. Thus Füchtbauer found that for the same intensity  $D_2$  is twice as strongly absorbed as  $D_1$ .

Up to the present time neither the physical basis of fine width of absorption lines has been cleared up, nor are we in possession of any formula for absorption applicable to all the lines of a series.

## 2.

The attempts which have been made to deal with the interaction between matter and radiation‡ may be broadly

\* Milne, in a note to 'Nature,' see Month. Notices R. A. S. June 1925.

† Foote & Mohler, Physical Review, xxvi. p. 195 (1925).

‡ See Month. Notices R. A. S. lxxxv. June 1925; the controversy between Milne and Stewart.

subdivided into two classes—(1) those based on the methods used in the kinetic theory of gases; (2) those based on thermodynamical methods. To the first category belong the works of Milne\* “On the Statistical Equilibrium in relation to Photoelectric Effect,” and of R. H. Fowler† “On Statistical Equilibrium and the Mechanism of Ionization by Electronic Impacts.” In these cases some knowledge or some assumption regarding the details of the unit mechanism of reaction is essential. Milne assumes that high temperature ionization is largely a volume photoelectric phenomenon, while Fowler treats the case where ionization is promoted by collision, in particular by electronic impacts. It may be mentioned that these methods follow on the lines initiated by Guldberg and Waage, Boltzmann, and J. J. Thomson in dealing with the problems of dissociation equilibrium and molecular aggregation‡. In the thermodynamical method, as developed by van’t Hoff, Nernst, Sackur§, and others, a knowledge of the detailed mechanism is not so indispensable.

The result is obtained by a treatment of the initial and final states, provided the net change in energy-content is known. The theory thereby loses somewhat in definiteness, but it has the compensating advantage of being free from the vagueness of the assumptions involved in the kinetic methods.

In the present paper we have followed Ehrenfest’s method of dealing with dissociation equilibrium. Attempts in this direction have already been made by R. H. Fowler||, Fowler and Milne¶, and by Becker\*\*. But they confined their attention to the production of metastable states.

Ehrenfest†† has shown that the behaviour of a mixture of gases in thermodynamical equilibrium can be defined by a function  $\{\gamma\}$  which may be regarded as the total phase-space described by the system. The function  $\{\gamma\}$  is allied to the familiar entropy function, but Ehrenfest did not trace the connexion between the two. In two previous papers‡‡, we have shown that  $\{\gamma\}$  is connected with Boltzmann’s

\* Milne, *Phil. Mag.* (6) xlvii. p. 209.

† R. H. Fowler, *Phil. Mag.* (6) xlvii. p. 257.

‡ For a summary, see Jeans, ‘*Dynamical Theory of Gases*,’ chap. 7, pp. 209–219.

§ See Sackur, ‘*Thermodynamics*,’ chap. 9.

|| Fowler, *Phil. Mag.* (6) xlv. p. 1.

¶ Fowler & Milne, *Month. Notices Roy. Ast. Soc.* lxxiii. p. 403.

\*\* Becker, *Zs. für Physik*, xviii. p. 325.

†† Ehrenfest & Trkal, *Proc. Amst.* xxi. (1920); *Ann. der Physik*, lxiii.

‡‡ Saha & Sur, *Phil. Mag.* Jan. 1926, p. 279.

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probability function  $W$ , by the relation :

$$W = \{\gamma\}/\{\gamma\}_0,$$

where  $\{\gamma\}_0$  = value of  $\{\gamma\}$  when the system is reduced to absolute zero of temperature.

This theorem holds not only for matter, but we showed in the second paper that it also holds for radiation. The entropy of radiation can be calculated from formula (1) by an extension of S. N. Bose's method \*.

This is equivalent to treating radiation as a new component in chemical equilibrium. A similar view has already been expressed by Smit; according to him the familiar phase-rule

$$F = C + 2 - P$$

has to be replaced in photochemical reactions by the rule  $C + 3 - P$ . The photochemically active light plays the rôle of a new component.

Turning to the present case, it is easy to see that a sodium atom with its electron in the  $2p$ -orbits or any higher orbit may be regarded as a chemical entity different from a normal Na-atom. The  $\text{Na}_{2p}$  atom may, for practical purposes, be regarded as compound of Na- (normal) and  $D_1, D_2$  pulses. Thus the lines of the sodium spectrum,  $\text{Na}^+$ -ion, and the electron may be regarded as the independent components out of which the whole system, consisting of normal atom  $\text{Na}^+$  and the metastable states of Na, are evolved.

### 3.

Let us now consider a system consisting of

$n_1$	.....	neutral atoms,
$n_2$	.....	ionized atoms,
$n_3$	.. .. .	free electrons.

Let  $n_1 + n_2 + n_3 = n$ , and  $K$  = kinetic energy of the material particles. Let  $N, d\nu$  = total number of quanta of frequency  $\nu$  comprised within the range  $d\nu$ . Then, according to the methods described in the previous papers,

$$W_{d\nu} \text{ for radiation} = \Pi \left\{ \frac{(A_s + N_s)!}{A_s! N_s!} \right\}^{d\nu} \quad (1)$$

\* S. N. Bose, *Zs. für Physik*, xxvi. p. 178 (1924); xxvii. p. 384.

For the material particles

$$W_p = \frac{\mu_1^{n_1}}{h^{3n_1} \cdot n_1!} \cdot \frac{\mu_2^{n_2}}{h^{3n_2} \cdot n_2!} \cdot \frac{\mu_3^{n_3}}{h^{3n_3} \cdot n_3!} \cdot \dots \quad (2)$$

We shall here ignore the motion of an electron about its nucleus, and suppose that each material particle has only three degrees of freedom, viz. those corresponding to the motion of translation along three mutually perpendicular axes. Therefore, we have,

$$\left. \begin{aligned} \mu_1 &= \int \dots dx dy dz \cdot dp_x dp_y dp_z \\ &= V \int \dots dp_x dp_y dp_z, \\ \mu_2 &= V \int \dots dp_x' dp_y' dp_z', \\ \mu_3 &= V \int \dots dp_x'' dp_y'' dp_z'', \end{aligned} \right\} \dots \quad (3)$$

$V$  = total volume of the gas, and  $p_x, p_y, p_z$ , etc. represent the momenta coordinates of the particles.

Hence

$$W_p = \frac{V^n}{h^{3n} n_1! n_2! n_3!} \int \dots dp_{1x} dp_{1y} dp_{1z} \dots dp_{1x}' dp_{1y}' dp_{1z}' \dots dp_{1x}'' dp_{1y}'' dp_{1z}'',$$

the integrals being taken for all molecules of each class. The total kinetic energy  $K$  being given, the integration is to be performed subject to the condition

$$\sum \frac{p_{1x}^2 + p_{1y}^2 + p_{1z}^2}{2M} + \sum \frac{p_{1x}'^2 + p_{1y}'^2 + p_{1z}'^2}{2M} + \sum \frac{p_{1x}''^2 + p_{1y}''^2 + p_{1z}''^2}{2m} = K, \quad (4)$$

where  $M$  = mass of a neutral atom and  $m$  = mass of an electron.

Thus

$$W_p = \frac{V^n}{h^{3n} \cdot n_1! n_2! n_3!} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left(\frac{3n}{2}\right)!} \cdot (\sqrt{M^3})^{n_1} (\sqrt{M^3})^{n_2} (\sqrt{m^3})^{n_3} \dots \quad (5)$$

For the total system, consisting of radiation and the material particles,

$$W = W_{dv} \cdot W_p,$$

or

$$W = \Pi \left\{ \frac{(A_s + N_s)!}{A_s! N_s!} \right\}^{dv} \cdot \frac{V^n}{h^{3n}} \cdot \frac{1}{n_1! n_2! n_3!} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left(\frac{3n}{2}\right)!} \cdot (\sqrt{M^3})^{n_1} (\sqrt{M^3})^{n_2} (\sqrt{m^3})^{n_3}. \quad (6)$$

Let us now consider a unit process in which a neutral atom is dissociated into a free electron and a positively charged atom by the absorption of a quantum  $h\nu$ . Then

$$\begin{aligned} n_1 &\text{ changes to } n_1 - 1 \\ n_2 &\text{ ,, ,, } n_2 + 1 \\ n_3 &\text{ ,, ,, } n_3 + 1 \\ n &\text{ ,, ,, } n + 1 \\ N_s dv &\text{ ,, ,, } N_s dv - 1. \end{aligned}$$

The total energy  $E$  of the combined system, however, remains unaltered, i. e.  $dE = 0$ ,

$$dE = dK + \chi - h\nu_s = 0,$$

or

$$dK = h\nu - \chi, \quad \dots \dots \dots (7)$$

where  $\chi$  represents the ionization potential per atom. The probability of the system now is

$$W' = \Pi \frac{(A_s dv + N_s dv - 1)!}{A_s dv! (N_s dv - 1)!} \cdot \frac{V^{n+1}}{h^{3(n+1)}} \cdot \frac{\{2\pi(K + dK)\}^{\frac{3(n+1)}{2}}}{(n_1 - 1)! (n_2 + 1)! (n_3 + 1)!} \cdot \frac{(\sqrt{M^3})^{n_1 - 1} (\sqrt{M^3})^{n_2 + 1} (\sqrt{m^3})^{n_3 + 1}}{\left(\frac{3(n+1)}{2}\right)!}. \quad (8)$$

For equilibrium,

$$dW = W' - W = 0, \quad \dots \dots \dots (9)$$

whence we obtain,

$$\begin{aligned} &\frac{1}{n_1} \cdot \frac{A_s dv + N_s dv}{N_s dv} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left(\frac{3n}{2}\right)!} \\ &= \frac{V}{h^3} \cdot \frac{1}{n_2 n_3} \cdot \frac{\{2\pi(K + dK)\}^{\frac{3(n+1)}{2}}}{\left(\frac{3(n+1)}{2}\right)!} \cdot m^{3/2}. \quad (10) \end{aligned}$$

Replacing  $\left[\frac{(3n)}{2}\right]$  by  $\left(\frac{3n}{2}\right)!$  and using Stirling's formula,

$$\frac{n_2 \cdot n_3}{n_1} = \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot \left\{ \frac{2\pi m K}{\frac{3n}{2}} \right\}^{3/2} \cdot \left(1 + \frac{dK}{K}\right)^{\frac{3n}{2}},$$

$$\frac{n_2 \cdot n_3}{n_1} = \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot \left\{ \frac{2\pi m K}{\frac{3n}{2}} \right\}^{3/2} \cdot \left(1 + \frac{3n}{2} \frac{dK}{K}\right). \quad (11)$$

Putting  $K = \frac{3n}{2} kT$ , and using (7), we have, after taking logarithms,

$$\log \frac{n_2 \cdot n_3}{n_1} = \frac{h\nu - \chi}{kT} + \log \left\{ \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot (2\pi m kT)^{3/2} \right\}. \quad (12)$$

Now

$$\frac{N_s}{A_s + N_s} = \frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu}. \quad (13)$$

Using partial pressures, we have, after some reduction,

$$\log \frac{p_2 \cdot p_3}{p_1} = \frac{N h \nu - U}{RT} + \log \frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu} + \frac{5}{2} \log T$$

$$+ \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}, \quad (14)$$

where  $N$  = Avogadro number,

$U$  = Ionization potential for a mol.

If the temperature of radiation be the same as that of the gaseous system

$$\rho_\nu = 8\pi \frac{h\nu^3}{c^3} \cdot \frac{1}{e^{\frac{h\nu}{kT}} - 1}, \quad (15)$$

the quantity  $\frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu}$  reduces to  $e^{-\frac{h\nu}{kT}}$ , and the equation

(14) reduces to the familiar form

$$\log \frac{p_2 \cdot p_3}{p_1} = -\frac{U}{RT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}. \quad (16)$$



If, within the reaction-space, the density of radiation be the same as that given within black-body chamber,

$$\frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu} = e^{-\frac{h\nu}{kT_s}},$$

where  $T_s$  = temperature of radiation.

Then

$$\log \frac{p_2 \cdot p_3}{p_1} = \frac{N h \nu}{R T} \left( \frac{1}{T} - \frac{1}{T_s} \right) - \frac{U}{R T} + \frac{1}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}. \quad (17)$$

This formula is practically identical with one given earlier by Einstein \*. Einstein's formula was deduced for photochemical reactions, and runs thus :

$$\log \frac{n_2 \cdot n_3}{n_1} = \frac{N h \nu}{R} \left( \frac{1}{T} - \frac{1}{T_s} \right) + \frac{1}{R} \sum \delta n \left\{ c_\nu \log T + c_1 - (c_\nu + R) - \frac{b_1}{T} \right\}. \quad (17')$$

It is easy to see that we can apply this formula directly to the present case and arrive at (17).

Formula (14) is, however, quite general and can be adapted to the circumstances of the case. In place of  $\rho_\nu$  we have now to use  $I_\nu$ , where  $I_\nu$  is the intensity of light from the source in the reaction-space. The formula then takes the form :

$$\log \frac{p_2 \cdot p_3}{p_1} = \frac{N h \nu - U}{R T} + \log \frac{I_\nu}{2 \frac{h\nu^3}{c^3} + I_\nu} + \frac{1}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}. \quad (18)$$

As a special case, let the radiation proceed from a black-body radiator at temperature  $T_s$ , and let the radiation be confined within a solid angle  $w$ . Let  $F_\nu$  be its residual intensity in the reaction-space, i. e.  $F_\nu = r \cdot I_\nu$ ,  $r$  being a fraction and

$$I_\nu = 2 \frac{h\nu^3}{c^3} \cdot \frac{1}{e^{\frac{h\nu}{kT_s}} - 1}.$$

\* Einstein, *Ann. der Physik*, xxxvii. p. 838.

The quantity  $\frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu}$  is to be replaced by  $\frac{r \frac{w}{4\pi} \cdot I_\nu}{2 \frac{h\nu^3}{c^3} + r \frac{w}{4\pi} I_\nu}$ ,

or to a first approximation by  $r \frac{w}{4\pi} e^{-\frac{h\nu}{kT_s}}$ .

The formula (14) then reduces to

$$\log \frac{p_2 \cdot p_3}{p_1} = \frac{N h \nu - U}{RT} + \log \left( r \frac{w}{4\pi} e^{-\frac{h\nu}{kT_s}} \right) + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}. \quad (18')$$

#### 4.

*Influence of Radiation in producing Higher Quantum States.*

By a similar treatment it is possible to deduce the equilibrium between normal and excited states. Let

$n_1$  = number of atoms in the normal state

(1s in the case of Na, 2p in the case of Al).

$n_2$  = number in any higher excited state

(2p in the case of Na).

$$n_1 + n_2 = n.$$

$N d\nu$  = number of energy pulses within the frequency region  $\nu, \nu + d\nu$ . The normal atoms pass to the excited state by the absorption of these pulses.

Then we have

$$W = \left\{ \frac{(A+N)!}{A! N!} \right\}^{d\nu} \cdot \frac{g_1^{n_1}}{h^{3n_1} \cdot n_1!} \cdot \frac{g_2^{n_2}}{h^{3n_2} \cdot n_2!} \cdot \frac{V^n}{\left( \frac{3n}{2} \right)} \cdot (2\pi K)^{\frac{3n}{2}} \cdot m^{\frac{3n}{2}};$$

$g_1$  and  $g_2$  represent the statistical weights of the two states,  $K$  the total kinetic energy, and  $m$  the mass of the atoms.

If we take a virtual displacement (unit change) in which  $n_1$  changes to  $n_1 - 1$ ,  $n_2$  to  $n_2 + 1$ , and  $N d\nu$  to  $N d\nu - 1$ , we have

$$W' = \frac{(A d\nu + N d\nu - 1)!}{A d\nu! (N d\nu - 1)!} \cdot \frac{g_1^{n_1-1} \cdot g_2^{n_2+1}}{h^{3n} \cdot (n_1 - 1)! (n_2 + 1)!} \cdot \frac{V^n}{\left( \frac{3n}{2} \right)} \cdot \{2\pi \overline{K + dK}\}^{\frac{3n}{2}} \cdot m^{\frac{3n}{2}},$$

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where  $dK = h\nu - \chi$ ;  $\chi$  now represents the difference in the energy levels of the two states.

Now putting

$$W' - W = 0 \quad \text{and} \quad K = \frac{3n}{2} kT,$$

we have

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot \frac{N}{A + N} \cdot \left(1 + \frac{h\nu - \chi}{kT}\right),$$

$$\text{or} \quad \frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot \frac{N}{A + N} \cdot e^{\frac{h\nu - \chi}{kT}} \quad \text{to an approximation,}$$

$$\text{i. e.} \quad \frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot \frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu} \cdot e^{\frac{h\nu - \chi}{kT}} \quad \dots \quad (19)$$

When the radiation is in temperature equilibrium with the gas, it is easy to see that

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot e^{-\frac{\chi}{kT}} \quad \dots \quad (20)$$

When  $T$  is sufficiently high

$$\frac{n_2}{n_1} = \frac{g_2}{g_1}, \quad \dots \quad (21)$$

as is apparent from the definition of weight factor.

#### *Conclusion.*

It will be seen from an inspection of the formulæ deduced that the finite breadth of the absorption band does not occur in any one of them. This shows that the formulæ can be regarded only as approximate. This is not unexpected, because the idea of absorption is rather foreign to the thermodynamical methods.

After a short note announcing this result was published in 'Nature' (Nature, April 11, 1923), Woltjer published a note in which he mentioned that the formulæ (14) and (19) could be obtained from Milne's method of treatment. We have found that this method gives identical results. But, contrary to our expectations, even in this method of treatment the absorption factor does not occur.

October 1, 1925.

**XCIII. The Dielectric Constants of Benzene Solutions.** By  
Prof. J. R. PARTINGTON, D.Sc., and J. F. J. RULE, B.Sc.\*

**T**HE dielectric constants of solutions of solids in non-ionizing solvents appear to have been little investigated, although those of several liquid mixtures have been determined (*e.g.*, by Philip, *Z. phys. Chem.* xxiv. p. 18, 1897; and Lange, *Z. Physik*, xxxiii. p. 169, 1925). Walden and his co-workers have investigated several conducting solutions (Walden, *Bull. Acad. St. Petersb.* vi. pp. 305 and 1055, 1912; *J. Am. Chem. Soc.* xxxv. p. 1649, 1913; Walden, Ulich and Werner, *Z. phys. Chem.* cxvi. p. 261, 1925; Ulich, *Z. Electrochem.* xxxi. p. 413, 1925).

In the present research, the dielectric constants of solutions of *m*-dinitrobenzene, phenol, and benzoic acid in benzene have been determined by the Nernst method (*Z. phys. Chem.* xiv. p. 622, 1894) as modified by Turner (*ibid.*, xxxv. p. 385, 1900).

It was found in the cases of *m*-dinitrobenzene and phenol that the dielectric constant of the solutions increased directly with concentration and seemed to approach the value of the pure solute in the *fused* state. Thus *m*-dinitrobenzene was found by Augustin (Diss. Leipzig, 1893) to have a dielectric constant of 2.85 when solid and 20.65 when fused at 90° C., whilst that of phenol when fused at 48° C. is 9.68 (Drude, *Z. phys. Chem.* xxiii. p. 267, 1897). The values extrapolated from our results are 30.5 for *m*-dinitrobenzene at 20° C., and 13.8 for phenol at 18° C. The curve for *m*-dinitrobenzene appears to decrease its gradient towards the higher concentrations, but the limitation of solubility would not allow of further investigation of the curve.

With benzoic acid the dielectric constant increased with concentration to a maximum and then decreased. No determination of the dielectric constants of benzoic acid appear to have been made. We have made a determination for solid benzoic acid by melting it in the dielectric trough and allowing it to crystallize, and found the value 1.7.

The trough in which the solutions were contained (Nernst, Turner, *loc. cit.*) was of brass and was at first nickel plated. It was found, however, that the benzoic acid solutions attacked the nickel slowly and the solution became green. This was overcome by well plating the trough with silver.

\* Communicated by the Authors.

The conductivity of the solutions was inappreciable, being no greater than that of benzene except in the case of phenol solutions at the higher concentrations.

The apparatus was calibrated by using benzene as a standard, the value of the dielectric constant of benzene being taken as 2.288 at 18° C (Turner, *loc. cit.*), which is the usually accepted value. Modern determinations of the dielectric constant of benzene, however, seem to point to a value of 2.24 (Sayce and Briscoe, *J. Chem. Soc.* cxxvii. p. 315, 1925, and Harris, *ibid.* cxxvii. p. 1049, 1925), but for the present the older value is retained.

### Materials.

**Benzene.**—Pure thiophen-free benzene of Kahlbaum was carefully dried over sodium and fractionally distilled. B.Pt. = 80°·5 C.  $D_4^{20} = 0.8779$ .

***m*-dinitrobenzene** prepared from benzene and nitric acid was crystallized twice from alcohol. M.Pt. = 80°·8 C.

**Phenol.**—British Drug Houses crystals which were used were found to be of good purity. They were distilled and the end portion rejected. M.Pt. = 40°·7 C. (M.Pt. of very pure phenol is 41°·5 C., Stratton and Partington, *Phil. Mag.* xliii. p. 436, 1922).

**Benzoic Acid.**—Pure chlorine-free acid was twice crystallized from water, dried, and then sublimed. M.Pt. = 121°·4 C.

### Results.

TABLE I.

*m*-dinitrobenzene in benzene. Temp. = 20° C.

Molec. Conc.	Per cent. Conc. by weight.	D.C.
0	0	2.286
0.088	1.66	2.32
0.176	3.31	3.34
0.264	5.05	3.95
0.351	6.55	4.24
0.423	7.55	4.68
0.562	9.83	5.57
0.628	11.19	5.91
0.742	12.95	6.51
0.842	14.44	7.22
1.007	16.62	7.59

Fig. 1—*m*-Dinitrobenzene in Benzene.

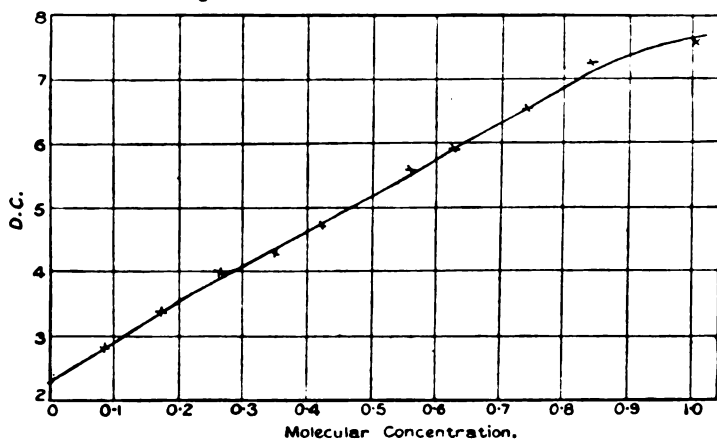


TABLE II.

Phenol in benzene. Temp. = 18° C.

Molec. Conc.	Per cent. Conc. by weight.	D.C.
0.00	0.00	2.288
0.700	7.73	2.64
0.951	12.48	2.80
1.40	15.23	3.08
1.90	19.66	3.37
2.82	26.61	4.02
3.85	33.14	4.62
5.57	41.34	5.61
6.55	45.74	6.25

Fig. 2.—Phenol in Benzene.

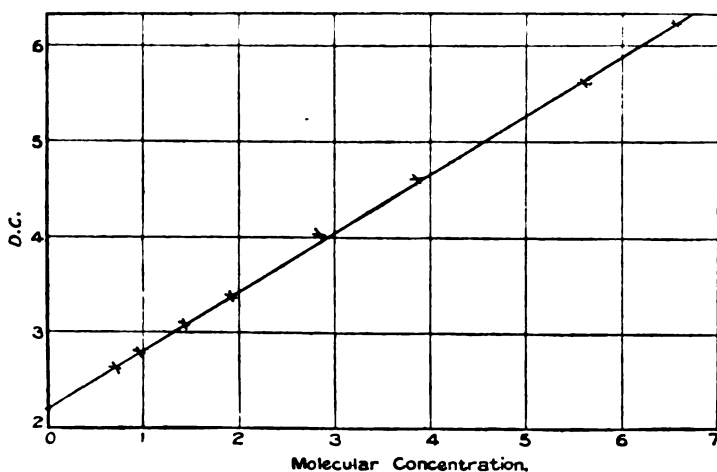
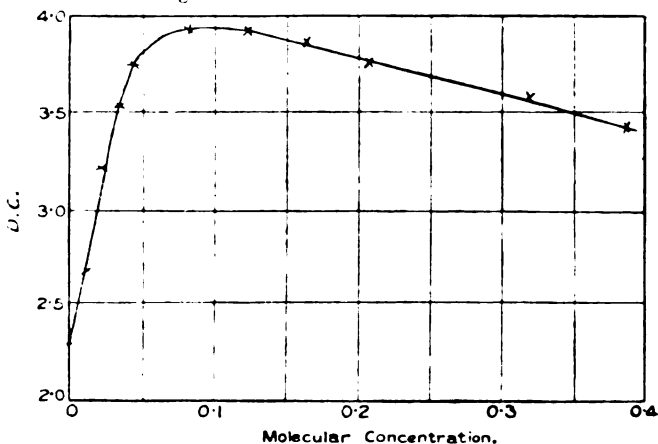


TABLE III.

Benzoic Acid in benzene. Temp. = 18° C.

Molec. Conc.	Per cent. Conc. by weight.	D.C.
0	0	2.288
0.011	0.15	2.67
0.023	0.30	3.22
0.035	0.46	3.53
0.043	0.61	3.76
0.082	1.11	3.94
0.123	1.69	3.93
0.164	2.24	3.87
0.205	2.81	3.74
0.322	4.44	3.57
0.393	5.38	3.43

Fig. 3.—Benzoic Acid in Benzene.

*Summary.*

1. The dielectric constants of solutions of *m*-dinitrobenzene, phenol, and benzoic acid in benzene were determined.

2. In the cases of *m*-dinitrobenzene and phenol the dielectric constant increased steadily with concentration and appeared to approach the value for the pure solute in the fused state.

3. In the case of benzoic acid, the dielectric constant increased with concentration to a maximum and then decreased.

We wish to acknowledge the receipt of a Research Grant from the Chemical Society to one of the authors (J.F.J.R.), which has defrayed part of the cost of the investigation.

The work is being extended to conducting solutions.

Chemistry Department,  
East London College,  
University of London.

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XCIV. *Lines of Maximum Principal Stress in Thin Mild Steel Plates of Rectangular Shape fixed along the Edges and uniformly loaded.* By B. C. LAWS, D.Sc., A.R.C.Sc., M.I.C.E., and A. O. ALLEN, M.A., B.Sc., A.R.C.Sc.\*

**S**TRESS distribution in thin disks fixed at their boundaries is not easy of determination—at least where the boundaries suffer abrupt changes in direction—whether the problem is approached from pure mathematical considerations or by the aid of experiment.

Both processes involve much labour. In the former certain assumptions may be made to facilitate the solution, but the results obtained are more or less unsatisfactory. Experimental investigation, however, provides data which under careful mathematical analysis produce results to which little objection can be raised.

The problem is not only of academic interest, but is commonly met with in certain classes of constructive engineering, and from both points of view the solution is of value.

Experiments were carried out in the Physics Department of the University of Leeds during the latter part of the war, and subsequently, upon rectangular-shaped plates of different thicknesses and dimensions fixed at their boundaries and subject to uniformly distributed loads.

An important part of the inquiry was to determine the value and position of "maximum stress," a knowledge of which has a very important bearing on certain practical problems. It formed the subject of a paper † by one of the authors, recently published, in which formulæ were obtained giving "maximum stress" and "maximum deflexion" in terms of the dimensions of the plate, its thickness, and the load imposed.

The inquiry is now carried a little further, and it has been sought to determine in what manner the stress varies from point to point and how the plate changes in form under the

\* Communicated by the Authors.

† Proceedings of the Institution of Civil Engineers, vol. ccxiii. part 1.



load. Several points of physical significance arise out of the analysis, and certain characteristics become evident which without the aid of experimental data can only be a matter of conjecture.

Microscopic observations of deflexions were made at the points of intersection of ordinates drawn on the plate surface parallel to the sides of the rectangle, and represented graphically. The first and second derived curves of the graphs were calculated by the "method of differences."

A check was placed on the curves of slope by observing the change of gradient of the plate by means of small mirrors mounted on a suitable table geometrically supported at the several points of observation and confirmed the near accuracy of the calculations.

The analysis was based on the following theoretical principles:—

If  $z=f(x, y)$  be the equation of the plate surface after deflexion referred to a datum plane situated midway between the initial plate surfaces, then the radii of principal curvature at  $(x, y, z)$  are respectively given by

$$\rho = \frac{t + r \pm \sqrt{(r-t)^2 + 4s^2}}{2(s^2 - r \cdot t)},$$

where

$$t = \frac{d^2 z}{dy^2}, \quad r = \frac{d^2 z}{dx^2}, \quad \text{and} \quad s = \frac{d^2 z}{dx \cdot dy},$$

the plate surface being assumed of small curvature.

The principal stresses due to bending have been calculated from the formulæ:

$$p_1 = \frac{\sigma \cdot E \cdot T}{2(\sigma^2 - 1)} \left( \frac{1}{\rho_2} + \frac{\sigma}{\rho_1} \right), \quad \text{and} \quad p_2 = \frac{\sigma \cdot E \cdot T}{2(\sigma^2 - 1)} \left( \frac{1}{\rho_1} + \frac{\sigma}{\rho_2} \right),$$

where  $\rho_1$  and  $\rho_2$  are the principal radii of curvature given above,  $\frac{1}{\sigma}$  = Poisson's ratio,  $E$  = Young's modulus, and  $T$  = the thickness of the plate.

The values of  $E$ , and Poisson's ratio, were determined by separate experiments on samples cut from the plates, and  $T$  by weighing the plates.

$r$ ,  $s$ , and  $t$  were obtained by differentiating twice the deflexion graphs represented by

$$z = a + \frac{x}{h} \cdot d_1 + \frac{x}{h} \left( \frac{x}{h} - 1 \right) \frac{d_2}{2!} + \frac{x}{h} \left( \frac{x}{h} - 1 \right) \left( \frac{x}{h} - 2 \right) \frac{d_3}{3!} + \dots$$

and  $z = a + \frac{y}{h} d_1 + \text{etc.}$ ,

in which the ordinates of the curve at any section are equally spaced at intervals " $h$ "; " $a$ " is the first term of a series of consecutive ordinates,  $d_1 d_2 d_3 \dots$  the first terms of the successive order of differences of the ordinates, and  $x$  (or  $y$ ) the abscissa value of any—the  $n$ th—ordinate  $z$  whereof  $x$  (or  $y$ ) =  $(n-1)h$ .

By the aid of the foregoing principles the variation of stress along the several sections was graphically represented to a suitable scale, and the graphs cut by lines (or planes) parallel to the initial plate surface at a height from the latter representing certain stress values, the intersections being then projected on to the plate surface and the loci of particular stress values obtained. The latter are shown in the accompanying diagram.

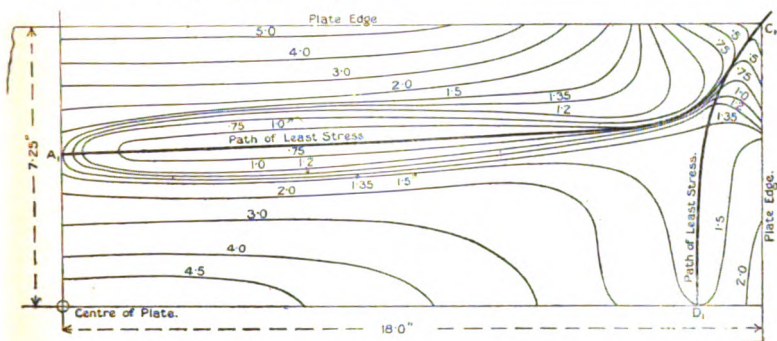


Diagram of "Lines of Maximum Principal Stress" for a thin mild steel plate 36 in.  $\times$  14.5 in.  $\times$  .244 in. thickness, fixed along its edges and subject to a load of .0045 ton per sq. inch of surface. Particular stress values in tons per sq. inch are indicated by numerals in the diagram.

The stress reaches a maximum at the middle point of the longer edges of the rectangle; it falls off slowly along the edge for a distance of about half its length and then quickly diminishes towards the corners of the rectangle where it approaches zero.

Along the axis through the centre of the plate parallel to the shorter side of the rectangle the stress diminishes to a comparatively small value at a distance from the plate centre depending upon the ratio between the sides of the rectangle, increasing again to a value at the centre of the plate less than that at the middle point of the longer side.

There is a similar variation along the shorter side and longer axis of the rectangle, but here the stress values generally are not so great.

The path pursued by a "particular stress value" is indicated in the diagram, an examination of which shows that the "lines of constant stress" follow each other in a very orderly manner.

The diagram refers to a plate 36 in.  $\times$  14.5 in. of thickness .244 inch, and subject to a hydrostatic load of .0045 ton per square inch of surface.

The thick lines  $A_1C_1$ ,  $D_1C_1$  in the diagram—drawn through the points of least stress in the several sections—may be termed the "path of least stress" for the plate. They correspond to nodal lines in a vibrating plate, and mark the demarcation between those portions of the plate, having opposite curvature, whereof the portions enclosed between them and the sides of the rectangle are of like curvature and opposite in sign to that of the area which they enclose in the body of the plate.

Had the plate been fixed independently along two parallel edges only so that the remaining edges are free, the path of least stress would obviously have been parallel to the former and correspond to the position of contraflexure in a simple beam fixed at its ends.

January 21, 1926.

XCV. *The Adsorption of Gases by Activated Charcoal at Very Low Pressures.*—II. At  $-183^\circ \text{C}$ . By H. ROWE, B.Sc., Demonstrator in Physics, University College of the South-West of England, Exeter\*.

### 1. INTRODUCTION.

IN previous experiments† the author has determined the quantitative adsorption of various gases by activated coconut charcoal at low pressures and  $20^\circ \text{C}$ ., and it was shown from these results that the adsorption isotherm is better represented by an equation of the type

$$\log_{10} \frac{\alpha}{P} = A_0 - A_1 \alpha \quad \dots \quad (1)$$

than by the equation which is usually quoted, viz.

$$\alpha = kP^{\frac{1}{n}}, \quad \dots \quad (2)$$

where  $\alpha$  = number of c.c., at N.T.P., adsorbed per gram of charcoal;

$P$  = pressure in cm. of mercury;

$A_0$ ,  $A_1$ ,  $k$ , and  $\frac{1}{n}$  are constants depending on the particular gas.

\* Communicated by Prof. F. H. Newman, D.Sc., A.R.C.S.

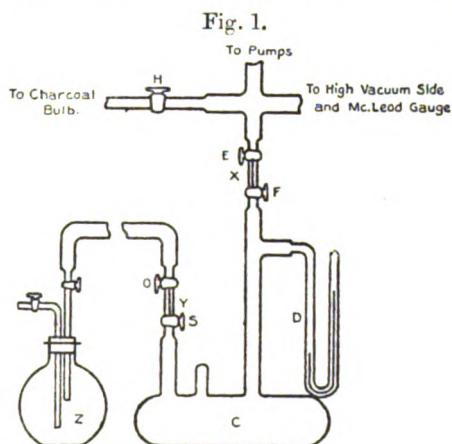
† Phil. Mag. li. p. 109 (1926).

It was found that at very low pressures the isotherm was not tangential to the volume axis, as is to be expected from a mathematical analysis of equation (2), but the tangent of the isotherm was of the same order of magnitude as that calculated from equation (1). Further, the relationship between  $\alpha$  and  $P$  was not linear except below pressures of the order  $10^{-3}$  mm., and in general the absolute value of this pressure varies with the boiling-point of the gas ; it decreases as the boiling-point increases.

It is well known that a lowering in the temperature of charcoal causes a very great increase in its adsorptive capacity, and measurements made at very low temperatures are more reliable than those made at air temperatures, because in the latter case only small quantities are adsorbed. The experiments previously described have therefore been carried to a further stage by determining the quantities of nitrogen, hydrogen, and carbon monoxide adsorbed when the activated coconut charcoal is maintained at  $-183^{\circ}$  C. by immersion of its containing-bulb in liquid oxygen.

## 2. EXPERIMENTAL ARRANGEMENT.

The apparatus used was similar to that employed previously, and the experimental procedure was similar except



for the method of introducing quantities of gas into the high vacuum side. It was found that admitting small volumes of gas by alternately opening and closing the taps F and E, measuring the pressure  $p_1$  in the high vacuum side, then admitting the gas to the charcoal and noting the final pressure  $p_2$ , practically all the gas was adsorbed, and no

appreciable increase in the equilibrium pressure within the limits of error of the experiment could be detected. Accordingly a modified method was adopted. The reservoir C was charged with gas from the containing-bulb Z, and its pressure read on the manometer D. Gas was then admitted to the high vacuum side, the tap H being closed, until the pressure in D fell to a desired level; the taps between C and the high vacuum side were then closed and the pressure in D read after it had become steady. From a knowledge of these pressures and the component volumes the new pressure in the high vacuum side could be calculated thus:—

Let

- $p_1'$  = original pressure in C in mm.;  
 $p_2'$  = final                   "                   "                   "  
 $p_2$  = original pressure in high vacuum side;  
 $p_1$  = final                   "                   "                   "                   "  
 $V$  = volume of high vacuum side;  
 $v$  = volume of C.

Then 
$$p_1 = \frac{v(p_1' - p_2')}{V} + p_2;$$

$$V = 3163 \text{ c.c.}; v = 128.5 \text{ c.c.};$$

$$p_1' - p_2' = \text{approx. 100 mm. of mercury};$$

$$p_1 \text{ was therefore of the order of 4 mm.}$$

The quantities of gas adsorbed were so large that it was found convenient to calculate them in c.c. at N.T.P.

Let

- $p_1$  = original pressure in high vacuum side;  
 $p_2$  = final                   "                   "                   "  
           after adsorption had taken place;  
 $\theta$  = temperature in ° C.;  
 $m$  = mass of charcoal in grams.

Then the quantity adsorbed per gram of charcoal in c.c. at N.T.P. is given by

$$\alpha = \frac{V(p_1 - p_2) \cdot 273}{m \cdot 760 \cdot (273 + \theta)}.$$

As in the previous experiments, it is assumed that the total quantity of gas,  $\alpha$ , in the charcoal at any given equilibrium pressure  $p$  is the sum of all the quantities adsorbed.

The equilibrium pressure  $p$  will not be equal to the final pressure  $p_2$  in the high vacuum part, as a correction must be applied for thermal diffusion; the charcoal, and the gas immediately surrounding it, is at a much lower temperature than the remainder of the apparatus. The equilibrium pressure at  $\theta^\circ \text{C.}$  is given by

$$p = p_2 \sqrt{\frac{90}{273 + \theta}}.$$

The temperature of liquid oxygen is taken as  $-183^\circ \text{C.}$

The same sample of charcoal was used for nitrogen, hydrogen, and carbon monoxide, but as it was suspected that the presence of the other gases affected the adsorptive capacity of the charcoal for hydrogen, a fresh sample of reactivated charcoal was used with this gas. In actual practice it was found that this fresh sample had a far larger adsorptive capacity for hydrogen than the one that had been used in the previous case.

### 3. EXPERIMENTAL RESULTS.

#### a. Nitrogen.

The nitrogen used in these experiments was prepared by a method suggested by Waran\*. When dilute ammonia is acted upon by bromine water, the resulting nitrogen is free from all impurities except water-vapour; this was removed by passing the gas over phosphorus pentoxide, and the bulb in which the gas was stored also contained a layer of phosphorus pentoxide.

In the initial adsorption, *i. e.* until the final pressure had reached the order of  $5 \times 10^{-4} \text{ mm.}$ , gas was admitted to the high vacuum side by small doses, but above this range so much nitrogen was necessary before the final pressure showed any appreciable increase that the modified method of introducing gas, described above, was used.

The charcoal bulb was surrounded by liquid oxygen for one hour before readings were commenced, otherwise it was found that the adsorption was erratic, due probably to inequalities of the temperature throughout the mass of charcoal.

At pressures lower than  $10^{-3} \text{ mm.}$  the time required for equilibrium to be attained was about 60 minutes, but at the highest pressures this time decreased considerably, and was 30 minutes at  $8 \times 10^{-2} \text{ mm.}$  This time-effect may be due to diffusion within the apparatus.

\* Phil. Mag. xlii. p. 246 (1921).

The air-temperature was noted at each pressure reading, and this value was used in calculating the quantity of gas adsorbed at N.T.P.

The results obtained with nitrogen are given in Table I.

TABLE I.  
Adsorption of Nitrogen at  $-183^{\circ}\text{C}$ .

$p$ . Equilibrium pressure.	$\alpha$ . Quantity of gas adsorbed at N.T.P.	$p$ . Equilibrium pressure.	$\alpha$ . Quantity of gas adsorbed at N.T.P.
$3.0 \times 10^{-6}$ mm.	0.223 c.c.	$9.72 \times 10^{-3}$ mm.	49.21 c.c.
6.4	0.336	13.11	54.48
$1.16 \times 10^{-4}$	1.095	18.60	60.73
2.67	2.539	22.58	65.78
4.69	4.318	31.09	70.82
8.15	8.832	46.06	75.13
$1.32 \times 10^{-3}$	13.54	55.99	77.33
1.99	22.14	70.30	79.77
4.38	39.11	79.75	81.31
6.66	44.16		

The relation between  $p$  and  $\alpha$  is shown by curve (a), fig. 2. At pressures below  $2.5 \times 10^{-3}$  mm. the relation is linear, and may be represented by

$$\alpha = kp. \quad \dots \dots \dots (3)$$

The results below  $7 \times 10^{-3}$  mm. are represented on a larger scale by curve (a), fig. 3.

The adsorption equation usually quoted,

$$\alpha = kP^{\frac{1}{n}}, \quad \text{where } P \text{ is in cm. of mercury,}$$

may be written in the form

$$\log \alpha = \log k + \frac{1}{n} \log P, \quad \dots \dots \dots (4)$$

and curve (a), fig. 4, shows the result of plotting  $\log_{10} \alpha$  and  $\log_{10} P$ . An examination of this curve shows that it consists of two parts, both of which are approximately straight lines.

The values of  $\frac{1}{n}$  for these portions have been determined; below  $2 \times 10^{-3}$  mm. it is 1.22, but above this point it changes to 0.20. This decrease of  $\frac{1}{n}$  with increase in equilibrium pressure is in agreement with the conclusion of Claude\* and Titoff†, and it was found that the adsorption isotherm given

\* *Comp. Rend.* xlviii. p. 861 (1914).

† *Zeits. Phys. Chem.* lxxiv. p. 641 (1910).

by the author's results is similar in form to that deduced from Claude's results, but the quantities adsorbed in the present experiments are greater.

Considering the relation between  $\alpha$  and  $P$  given in equation (1) and plotting  $\log_{10} \frac{\alpha}{P}$  against  $\alpha$  as shown by curve (a), fig. 5, there is a linear relation between these latter quantities above  $2 \times 10^{-3}$  mm. pressure; below this pressure the relation is represented by a straight line parallel to the  $\alpha$  axis, and this is to be expected if within the pressure range the relation between  $\alpha$  and  $P$  is a linear one. The value of  $A_0$  given by the horizontal portion is 5.0012.

### b. Hydrogen.

Hydrogen was prepared by the electrolytic decomposition, between platinum electrodes, of freshly-boiled distilled water, acidified with pure concentrated sulphuric acid. The gas was passed over phosphorus pentoxide and stored.

The charcoal which had been used in the adsorption of nitrogen was outgassed by heating to  $450^\circ$  C. for 12 hours, the pumping arrangements maintaining the pressure below  $10^{-5}$  mm. during the outgassing. Hydrogen was then admitted and, as in the case of nitrogen, a definite time was required for equilibrium to be attained, this time-interval decreasing as the pressure increased.

The results obtained for hydrogen are shown in Table II.

TABLE II.  
Adsorption of Hydrogen at  $-183^\circ$  C.

$P$ . Equilibrium pressure.	$\alpha$ . Quantity of gas adsorbed at N.T.P.	$P$ . Equilibrium pressure.	$\alpha$ . Quantity of gas adsorbed at N.T.P.
$7.00 \times 10^{-4}$ mm.	0.0046 c.c.	$23.59 \times 10^{-3}$ mm.	0.325 c.c.
9.44	0.0073	35.33	0.394
$1.51 \times 10^{-3}$	0.0122	40.47	0.461
2.57	0.0231	46.09	0.515
3.40	0.0304	49.01	0.554
4.25	0.0403	54.06	0.604
5.83	0.0563	57.92	0.656
8.07	0.0781	62.70	0.708
12.21	0.126	68.67	0.760
15.72	0.170	73.00	0.806
19.36	0.212	77.83	0.857
22.81	0.255		



The adsorption isotherm is shown at (b), fig. 2. The isotherm appears to be a straight line and the relation

Fig. 2.

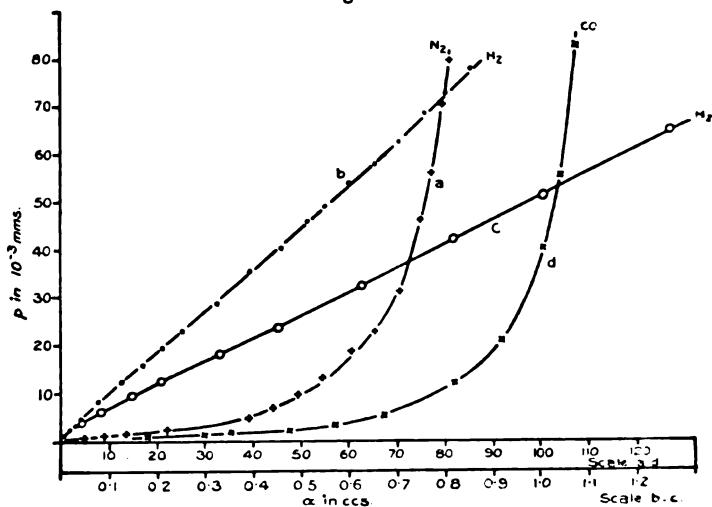
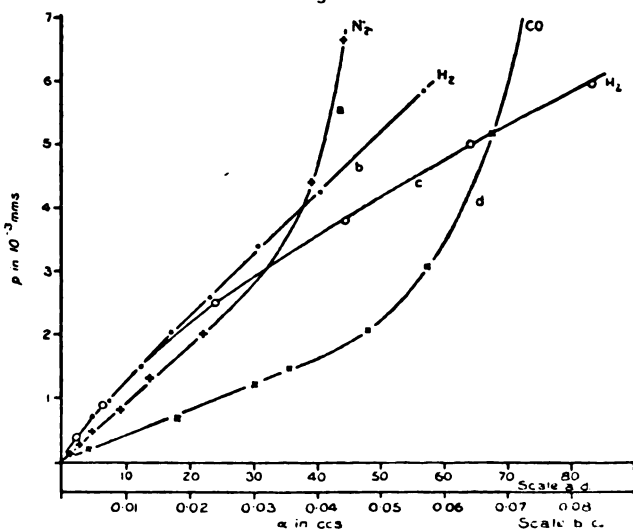


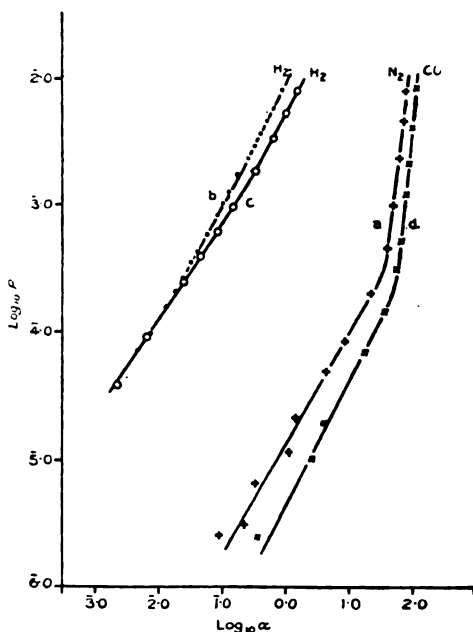
Fig. 3.



between  $\alpha$  and  $p$  is approximately a linear one, but when the scale is increased, as shown at (b), fig. 3, the isotherm

becomes convex to the pressure axis at pressures below  $5 \times 10^{-3}$  mm.

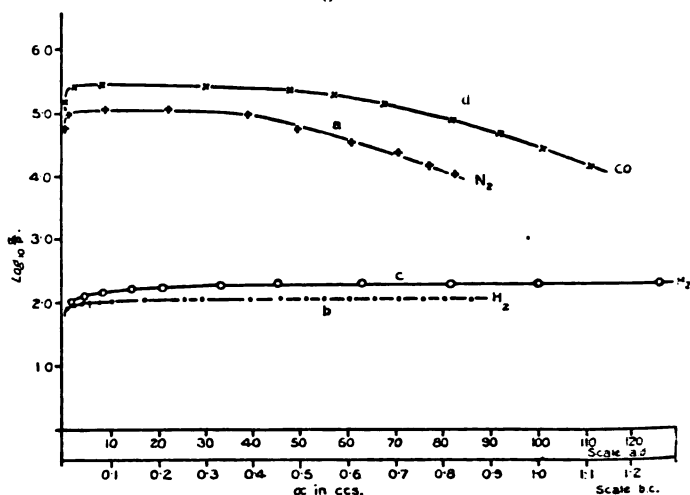
Fig. 4.



Since the relation between  $\alpha$  and  $p$  is so nearly linear, it is to be expected that a graph showing  $\log_{10} \alpha$  and  $\log_{10} P$  would be a straight line as in (b), fig. 4. The value of  $\frac{1}{n}$ , deduced from this line, is 1.08, and is in close agreement with Titoff's statement that  $\frac{1}{n}$  for hydrogen is unity at all pressures and temperatures. Similarly,  $\log_{10} \frac{\alpha}{P}$  is constant and therefore is represented in (b), fig. 5, by a line parallel to the  $\alpha$  axis. The value of  $A_0$  from this graph is 2.0376.

The quantities of hydrogen adsorbed, as shown in Table II. are smaller than those obtained by Claude. It was suspected that the low results were due to gas previously adsorbed by the charcoal, and accordingly a sample of freshly reactivated charcoal which was initially thoroughly outgassed was used.

Fig. 5.



The values obtained with this second sample are given in Table III.

TABLE III.

Adsorption of Hydrogen at  $-183^{\circ}\text{C}$ .

$p$ . Equilibrium pressure.	$a$ . Quantity of gas adsorbed at N.T.P.	$p$ . Equilibrium pressure.	$a$ . Quantity of gas adsorbed at N.T.P.
$3.72 \times 10^{-4}$ mm.	0.0021 c.c.	$18.04 \times 10^{-3}$ mm.	0.333 c.c.
8.91	0.0062	23.64	0.453
$2.50 \times 10^{-3}$	0.0239	32.47	0.629
3.79	0.0446	42.12	0.821
5.95	0.0836	51.31	1.009
9.40	0.146	65.10	1.274
12.39	0.208	80.72	1.539

In these second experiments the volumes adsorbed are about 75 per cent. greater than those previously obtained.

The isotherms for hydrogen are shown at (c) in figs. 2 and 3, and the  $\log_{10}$  relations at (c) in figs. 4 and 5. At pressures above  $10^{-2}$  mm. there is a linear relation between  $p$  and  $a$ , but below this pressure the isotherm is convex to the pressure axis, even more so than in the first results for hydrogen. At pressures higher than  $2 \times 10^{-2}$  mm. the value of  $\frac{1}{n}$ , deduced from the curve (c), fig. 4, is 1.02. Below

this pressure the slope becomes less until curves (b) and (c) coincide; the value of  $\frac{1}{n}$  for this portion is 1.03. The  $\log_{10} \frac{\alpha}{P}$  curve possesses the same characteristics as the former hydrogen curve, becoming a straight line parallel to the  $\alpha$  axis above  $2 \times 10^{-2}$  mm. and giving a value for  $A_0 = 2.2842$ .

c. Carbon monoxide.

This gas was prepared by the action of warm concentrated sulphuric acid on formic acid. The evolved gases were first passed through a wash-bottle and scrubbing-chamber containing concentrated caustic potash solution which removed formic acid gas, and water-vapour was eliminated by passing the carbon monoxide over phosphorus pentoxide.

This gas was admitted to the charcoal in a manner similar to that adopted with nitrogen, and a "time-effect" was observed, due probably to diffusion, although the possibility of a time-effect within the charcoal itself is not to be excluded.

The results are given in Table IV.

TABLE IV.

Adsorption of Carbon Monoxide at  $-183^\circ$  C.

<i>p.</i> Equilibrium pressure.	<i>a.</i> Quantity of gas adsorbed at N.T.P.	<i>p.</i> Equilibrium pressure.	<i>a.</i> Quantity of gas adsorbed at N.T.P.
$2.4 \times 10^{-5}$ mm.	0.339 c.c.	$3.08 \times 10^{-3}$ mm.	57.17 c.c.
9.8	2.475	5.17	67.53
$1.87 \times 10^{-4}$	4.007	11.80	81.88
6.77	17.96	20.75	91.82
$1.20 \times 10^{-3}$	30.01	40.24	100.96
1.46	35.33	55.68	104.75
2.08	47.78	83.01	111.23

The adsorption isotherm (d), fig. 2, is similar to that for nitrogen, but the pressure below which the curve becomes a straight line is slightly less, being  $1.5 \times 10^{-3}$  mm.

The graph showing the connexion between  $\log_{10} \alpha$  and  $\log_{10} P$  (b), fig. 4, consists of two portions; the value of  $\frac{1}{n}$  for pressures below  $1.5 \times 10^{-3}$  mm. is 1.41, but changes rapidly to 0.21 for higher pressures. The curve shown at (d), fig. 5, is similar to the corresponding nitrogen curve, the value of  $A_0$  for the horizontal portion being 5.3830.

## 4. DISCUSSION.

The adsorption isotherms are similar in shape to those obtained by other experiments working at higher temperatures and pressures. The nitrogen isotherm, at first straight, becomes concave to the pressure axis as the pressure increases. In this respect it differs from the isotherm at air-temperature, discussed in the previous paper, in which it was found to be convex to the pressure axis. The carbon-monoxide isotherm is similar to that for nitrogen. The hydrogen isotherm for charcoal which had been used in previous experiments is a straight line over practically the whole range of pressures used, but when drawn to a larger scale shows a slight convexity to the pressure axis at the lowest pressures. The isotherm for hydrogen using a fresh sample of reactivated charcoal has this convexity for a greater pressure range.

In all cases the quantities of gas adsorbed increase with their boiling-points.

At pressures below a critical pressure, which varies for the three gases, the adsorption isotherm is represented by

$$\alpha = kP$$

$$\text{or} \quad \log_{10} \frac{\alpha}{P} = A_0.$$

This critical pressure is comparatively high for the gases of low boiling-point, but is considerably lower for those gases of higher boiling-point and which are more readily adsorbed by charcoal. Its value for nitrogen and carbon monoxide is  $2.0 \times 10^{-3}$  mm. and  $1.5 \times 10^{-3}$  mm. respectively. Hydrogen shows anomalous results, as even at high pressures the isotherm is a straight line,  $\frac{1}{n}$  being equal to unity.

The value of the slope of the adsorption isotherm at the origin, derived mathematically from equation (1), is given by

$$\frac{dP}{d\alpha} = e^{-2.303 A_0} . . . . . (4)$$

The value of  $\frac{dP}{d\alpha}$  calculated from equation (4) is  $9.97 \times 10^{-6}$  for nitrogen, while the value obtained from the isotherm shown in fig. 3 is  $9.40 \times 10^{-6}$ . The calculated and experimental values of this constant for hydrogen are  $9.17 \times 10^{-3}$  and  $8.88 \times 10^{-3}$  respectively, and for carbon monoxide  $4.14 \times 10^{-6}$  and  $3.92 \times 10^{-6}$  respectively. In the above

calculation the value of  $A_0$  has been deduced from the horizontal part of the curves in fig. 5, as this corresponds to the linear relationship shown in the isotherms.

It was found that both at  $-183^\circ \text{C.}$  and at air-temperature a minimum equilibrium pressure is necessary before  $\log_{10} \frac{\alpha}{P}$  becomes constant ; below this minimum pressure, the value of which varies with the different gases, the value of  $\log_{10} \frac{\alpha}{P}$  increases with rise of pressure. This change cannot be explained, but it is present in all the gases so far examined at air-temperature as well as at  $-183^\circ \text{C.}$  It appears to be due to some physical property of adsorption at very low pressures. If  $\log_{10} \frac{\alpha}{P}$  increases with  $\alpha$  the adsorption isotherm must be convex to the pressure axis at these values, but the deviations from the linear relation at pressures below  $10^{-4} \text{ mm.}$  are not sufficient to state definitely that this is the case for nitrogen or carbon monoxide, although there is a definite convexity in the hydrogen curves.

As stated by Lamb, Wilson, and Chaney\*, adsorption represents a balanced condition between the free-gas space and the surface film. The higher the concentration of free gas the greater will be the quantity adsorbed. The amount of adsorption as shown in fig. 2 is not in all cases, however, strictly proportional to the pressure. The lower parts, where a considerable amount of gas is adsorbed with very small increase in pressure, very probably represents the amount of gas adsorbed in a layer one molecule deep covering the active surface of the carbon.

That part of the curve which is concave to the pressure axis very probably represents the amount of gas which is held by the less firm and more variable adsorption of molecules in the second and third layers, and the tenacity of this adsorption depends to a considerable extent upon the curvature of the capillaries within the carbon.

One c.c. of carbon monoxide at N.T.P. spread in a layer one molecule deep so that the molecules are in contact with one another in a square formation occupies a surface area of 2.76 sq. metres. The adsorption isotherm for carbon monoxide begins to show a decided change in curvature

\* Journ. Ind. & Eng. Chem. ii. p. 420 (1919).

after about 70 c.c. of gas at N.T.P. per gram. of charcoal have been adsorbed. Therefore, if this quantity is of unit molecular depth on the active surface of the charcoal, the minimum area occupied by it is 193 sq. metres. This value appears reasonable in view of the fact that activated charcoal has an estimated surface area of 2500 sq. metres per gram.

The shape of the adsorption isotherms can therefore be explained on the hypothesis given above. In the case of nitrogen and carbon monoxide the linear relationship holds until a layer one molecule deep is completed over the active surface, and the departure from this linear relationship represents the filling of the capillaries with layers of gas two and three molecules deep. The quantity of hydrogen adsorbed at the highest pressures in these experiments was not enough to saturate the molecular layer, and hence the isotherm remains a straight line over the whole range of pressures used.

## 5. SUMMARY.

1. Results have been obtained for the adsorption of nitrogen, hydrogen, and carbon monoxide at very low pressures and  $-183^{\circ}\text{C}$ .

2. The adsorption isotherms have the same characteristics as those at higher pressures, and are better represented by

$$\log_{10} \frac{\alpha}{P} = A_0 - A_1 \alpha$$

than by

$$c = kP^{\frac{1}{n}}.$$

3. The connexion between  $\alpha$  and  $P$  departs from a linear relationship after the active surface of the charcoal has been covered with a layer of gas of unit molecular depth.

In conclusion the author wishes to express his sincere thanks to Prof. F. H. Newman for suggesting this branch of research, and for the keen interest he has taken and the helpful suggestions made throughout.

**XCVI. *Estimates of Geological Time, with Special Reference to Thorium Minerals and Uranium Haloes.* By ARTHUR HOLMES, A.R.C.S., D.Sc., F.G.S., The University, Durham\*.**

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Conclusions.

*Introduction.*

**P**ROF. JOLY'S recent work, conveniently summed up in 'The Surface History of the Earth' (1925), raises the question of geological time in an acute form. Joly suggests that geological history is made up of four or five successive cycles of basaltic fusion and consolidation. Each of these may, he thinks, have involved from 40 to 60 million years, giving a total of from 160 to 300 million years. It is then claimed that these figures are supported by the method of finding the age of the oceans from denudational statistics. By making certain assumptions the sodium method gives, according to Sollas, 175 million years as a maximum †. It is also suggested that the accumulation of thorium-lead in thorium minerals is more likely to give a trustworthy age determination than that of uranium-lead in uranium minerals. Joly refers to a thorite from the Palæozoic pegmatites of the Langesundfjord which revealed an age of only 150 million years ‡, and he states that thorium-lead ratios would probably indicate about 250 million years for all geological time. Against the greater ages calculated from analyses of uranium minerals it is urged that in remote times uranium may have disintegrated more rapidly than it does to-day. Support for this view is sought in measurements of uranium haloes in mica from granites of different geological periods. The older haloes are found to have a greater radius than the younger, whereas in the case of thorium haloes no such anomaly has been detected.

\* Communicated by the Author.

† Q. J. G. S. vol. lxv. p. ciii (1909).

‡ See Table I., Analysis 9, and p. 1059 for comment.



While it is clear that the above results do not agree very happily among themselves, they do, nevertheless, favour comparatively low estimates of geological time, and they are definitely opposed to the longer estimates that have become familiar since Boltwood first suggested that lead might be the end-product of uranium. Evidently the whole of the data deserves a careful scrutiny, and I propose in this paper to examine it afresh.

### *Solvent Denudation.*

The determination of the age of the oceans by the well-known sodium method has been widely discussed, and many geologists have rejected it as worthless\*. In 'The Age of the Earth' (1913), I discussed the matter fully, and showed that the rocks would have to lose more sodium than they had ever contained in order to supply the amounts alleged to have been carried to the oceans by the rivers. So far as I know, no attempt has yet been made to refute this destructive argument.

For all the drainage areas of the world the estimated figures are as follows.—

Material carried annually to the Oceans.	Millions of Tons.
As sediment .....	5,700
In solution .....	2,440
<b>Total.....</b>	<b>8,140</b>
<b>Sodium in solution .....</b>	<b>156</b>

The sodium thus represents 1·9 per cent. of the material brought into the oceans. Of this material rather less than 90 per cent. is derived by erosion from the lands. The balance comes from the atmosphere and natural waters. The sodium therefore amounts to 2·1 per cent. of the material removed from the lands, according to denudational statistics.

The parent rocks of the eroded material consist of igneous and other crystalline rocks over roughly one-quarter of the area, and of sedimentary rocks over three-quarters of the area. The average sodium percentages in these rocks,

\* J. W. Gregory: 'Nature,' Oct. 27, 1921, p. 283. A Harker: Proc. Yorkshire Geol. Soc. xix. p. 9 (1914). T. C. Chamberlin: Proc. Am. Phil. Soc. lxi. pp. 255-271 (1922). J. Barrell: Bull. Geol. Soc. Am. xxviii. p. 838 (1917).

according to the latest figures given by Clarke and Washington \*, are :—

Igneous, 2·85 per cent.	} Average for the whole area,
Sedimentary, 0·81 per cent.	

Even if metamorphic rocks contained as much sodium as igneous rocks, which they do not ; and if all the crystalline rocks were to be denuded as rapidly as sedimentary rocks, which they are not ; and if all rocks were to lose all their sodium, which they do not ; then the total amount of sodium lost could not exceed 1·32 per cent. Actually they cannot lose on an average more than about 1 per cent. Yet river analyses imply a loss that is at least twice as great.

There are two ways, not mutually exclusive, of explaining away the obvious contradiction. Either the sodium in river waters is largely cyclic (and the invariable presence of chlorine supports this view), or the analyses of river waters for sodium are misleading. Sodium in the minute quantities present in river waters would be very difficult to estimate exactly, even if the utmost care were taken. It cannot be determined directly, but only as a final remainder estimated by difference, and the tendency of the errors is to give results uniformly too high. Whatever may be the reason, the estimate of the sodium carried to the ocean is certainly wrong. The method of determining the age of the oceans in which this estimate is the determining factor is at present based on utterly unreliable data ; and whether or not the method be sound in principle, the results derived from it cannot be allowed to carry any weight in settling the question of geological time.

#### *The Accumulation of Lead in Thorium Minerals.*

It is now well known that an isotope of lead (atomic weight 206) is the end-product of the uranium-radium series of elements, and that another isotope of lead (atomic weight 208) is the end-product of the thorium series. In primary uranium minerals the ratio of lead to uranium is approximately constant for minerals of the same geological age ; while in minerals of different geological ages, the older the minerals the higher are the lead-ratios. On the assumption that uranium has always disintegrated at the same rate as we find it to do to-day, the age of a uranium

\* U.S. G. S. Prof. Paper, No. 127, 1924.

mineral is given to a first approximation by  $\frac{\text{Pb}}{\text{U}} \times 6,600$  million years. In thorium minerals, however, the ratio of lead to thorium follows no ascertainable rule. Theoretically the age of a thorium mineral is given by  $\frac{\text{Pb}}{\text{Th}} \times 18,000$  million years, or, reducing to the same factor as is used for uranium minerals,  $\frac{\text{Pb}}{0.37\text{Th}} \times 6,600$  million years. Some thorium minerals give the same ages as uranium minerals of the same geological age, but generally they give lower results which are discordant among themselves. In most radioactive minerals both uranium and thorium are present, and the age should therefore be given more accurately by taking both into consideration and using the formula  $\frac{\text{Pb}}{\text{U} + 0.37\text{Th}} \times 6,600$  million years\*.

The variability in the amount of lead accumulated in thorium minerals of the same age has been a serious stumbling-block in the development of the radioactive methods of measuring geological time. In 1914, Dr. R. W. Lawson and I concluded from the evidence then available that lead could not be the end-product of thorium†. We suggested thallium as an alternative. Professor Soddy later suggested that only 35 per cent. of the lead might be stable, and that the remainder might disintegrate into thallium‡. Later work has disproved both these hypotheses, and it is now generally accepted that all the lead produced from thorium is stable.

In 1917 Lawson attempted to explain the discrepancies by assuming that thorium minerals are in many cases secondary products, and consequently younger than the primary minerals with which they are associated§. The assumption, however, involves a geological improbability, and implies the action of a variable process which is difficult to formulate.

A somewhat different explanation is presented in this paper, but before discussing it, let us turn to the evidence of the minerals themselves.

TABLE I.—The minerals listed here are from the pegmatites associated with the nepheline-syenites of the Langesundfjord, thought by Brögger to be of Devonian age.

\* The contraction m.y. is used hereafter.

† Phil. Mag. Dec. 1914, p. 824; and May 1915, p. 673.

‡ 'Nature,' Feb. 15, 1917, p. 469; and May 24, 1917, p. 244.

§ Wien. Ber. cxxvi. p. 721 (1917).

TABLE I.—Thorium Minerals of Devonian age from the neighbourhood of Brevik, Langesundfjord, Norway.

Ref.	Mineral.	U.	Th.	Pb.	Th/U.	Pb/(U+0.37Th).
1.	Uranothorite.	10.104	14.20	0.428	1.4	0.028
2.	Uranothorite.	8.93	44.24	0.297	4.9	0.012
3.	Uranothorite.	8.70	44.04	0.335	5	0.013
4.	Thorite.	1.48	51.84	0.76	35	0.036
5.	Thorite.	1.42	51.04	0.745	36	0.036
6.	Orangite.	1.183	45.03	0.054	38	0.003
7.	Orangite.	1.244	49.44	0.057	40	0.003
8.	Orangite.	1.02	63.05	0.82	62	0.034
9.	Thorite.	0.45	30.10	0.35	67	0.031
10.	Thorite.	0.70	47.25	0.076	68	0.004
11.	Thorite.	0.72	49.43	0.081	70	0.004
12.	Thorite.	0.407	29.20	0.020	72	0.002

1, 6, 7, 10, 11, 12. Phil. Mag. Dec. 1914, p. 832.

2, 3, 4, 5, 8. Dana's 'Mineralogy,' 6th Ed., p. 488.

9. Fajans: *Zeit. f. Elektro-Chem.* xxiv. p. 189 (1918).

The lead-ratios vary widely, and show no relation to the relative abundance of thorium. This is shown by the last two columns. Now if, as Joly supposes, uranium disintegrated much more rapidly in the past than it does to-day, then, in any series of the same age, the minerals relatively rich in uranium should give higher lead-ratios than those poorer in uranium but richer in thorium. The actual results give no support to the assumption favoured by Joly. The wide variability of the relations suggests the action of some process that has affected certain minerals and certain specimens more than others. There is only one kind of geological process which would have the observed consequences, and that is the partial leaching out of lead from the minerals concerned by weathering or by ground-waters.

Lead separated from the thorite analysed by Fajans (No. 9) was found by Honigschmid to have an atomic weight of 207.90. This is the mineral from which Joly calculates the age of the Devonian pegmatites as 150 m.y., although according to the ratio here given, 0.031, the age would be 205 m.y. On the assumption of integral atomic weights for thorium-lead and uranium-lead, the atomic weight, 207.90, would imply that the lead separated from the mineral consisted of 5 per cent. uranium-lead and 95 per cent.

thorium-lead. The age can now be calculated from each of the two isotopes :—

No. 9.—

$$\left. \begin{array}{l} \frac{\text{Uranium-lead}}{\text{U}} \times 6,600 = 0.039 \times 6,600 = 257 \text{ m.y.} \\ \frac{\text{Thorium-lead}}{\text{Th}} \times 18,000 = 0.011 \times 18,000 = 198 \text{ m.y.} \end{array} \right\}$$

These results might be held to suggest either that uranium disintegrated more rapidly in the past, or that by leaching the mineral has lost more thorium-lead than uranium-lead. Unreasonable as the second alternative may seem to be at first sight, there are grounds for adopting it as being the hypothesis that on the whole coördinates the data most successfully.

Evidently the lead-ratios of Table I. are too variable to hold out any promise of a good determination. They seem to be, indeed, in the same position as the helium-ratios determined by Lord Rayleigh, which necessarily give only minimum results. The ratio 0.039 calculated from the uranium-lead of thorite No. 9 is likely to give the closest approach to the true age, though, if leaching has taken place, even this may be a minimum. It is noteworthy that other minerals from the same pegmatites but richer in uranium give ratios that average about 0.04\*.

TABLE II.—Most of the specimens of thorites and thorianites from Ceylon have been collected from gravels in which they are naturally concentrated. The minerals have, however, also been found *in situ* in certain pegmatites. These intrusions are younger than a group of zircon-bearing granites (Middle Pre-Cambrian age, lead ratio 0.16)†, which in turn are younger than the basal complex of crystalline limestones and gneisses. From a comparison of the Ceylon sequence with that of India, and that of East Africa, it seems most probable that the thorium pegmatites are of late Pre-Cambrian age, though the geological evidence does not preclude an early Palæozoic age. So far as is known, however, the minerals of Table II. are all of the same age, whatever that may be.

As in Table I., we find that the lead-ratios vary widely, from 0.017 to 0.075. The variation is independent of the proportion of thorium to uranium, though it is noteworthy that the thorites give lower ratios than the thorianites and are more variable among themselves.

\* A. Holmes and R. W. Lawson : *Phil. Mag.* Dec. 1914, p. 832.

† A. Holmes and R. W. Lawson : *Phil. Mag.* Dec. 1914, p. 836, Analysis No. 9. A. Holmes : *Q.J. G. S.* lxxiv. p. 86 (1918).

TABLE II.—Thorium Minerals (and Pitchblende) from Ceylon. Age: Upper Pre-Cambrian or Palæozoic.

Ref.	Mineral.	U.	Th.	Pb.	Th/U.	Pb/(U × 0·37 Th).
1.	Thorianite.	27·8	51·7	2·38	1·9	0·051
2.	„	26·8	57·0	3·5	2·1	0·073
3.	„	21·21	45·05	2·77	2·2	0·073
4.	„	24·8	54·9	2·16	2·2	0·048
5.	„	23·75	55·9	2·70	2·4	0·061
6.	„	23·0	55·0	2·78	2·4	0·064
7.	„	20·2	62·7	3·11	3·1	0·072
8.	„	13·1	67·3	1·87	5·1	0·049
9.	„	11·1	60·3	2·3	5·4	0·069
10.	„	11·8	68·9	2·34	5·8	0·063
11.	„	12·8	69·4	2·42	5·9	0·062
12.	„	11·4	69·5	2·36	6·1	0·063
13.	„	10·42	67·1	2·66	6·4	0·075
14.	„	9·5	63·7	2·10	6·7	0·063
15.	Thorite.	4·57	62·80	1·28	14	0·046
16.	„	3·50	59·2	0·78	17	0·030
17.	„	1·62	54·4	0·36	34	0·017
18.	„	1·88	65·38	1·71	35	0·065
19.	Pitchblende.	71·40	7·86	4·75	0·1	0·066

- 1, 4, 5, 6, 12. Analyst, Jones: *Proc. Roy. Soc. A*, lxxvii. p. 546 (1906).  
 2, 7, 10. „ Honigschmid: Privately communicated.  
 3, 18. Col. Reports, Misc. No. 74, Ceylon Cd. 5390 (1910).  
 8. Analyst, Ramsay: 'Nature,' lxi, p. 559 (1904).  
 9. „ Buchner: 'Nature,' lxxv, p. 165 (1906).  
 11, 13, 14. „ Blake: *Proc. Roy. Soc. A*, lxxvi. p. 253 (1905).  
 15, 16. Col. Reports, Misc. No. 87, Ceylon Cd. 7175 (1914).  
 17. Analysts, Soddy & Hyman: *Trans. Chem. Soc. cv*. p. 1404 (1914).  
 19. Col. Reports, Misc. No. 37, Ceylon, Cd. 3190, p. 38 (1906).

The three thorianites analysed by Honigschmid (Nos. 2, 7, and 10) are of special interest, as they represent the actual materials from which three samples of lead were extracted for atomic weight determination. The results obtained by Honigschmid\* were:—

Lead from No. 2, 206·84 (58% uranium-lead plus 42% thorium-lead).

Lead from No. 7, 206·91 (54·5% uranium-lead plus 45·5% thorium-lead).

Lead from No. 10, 207·21 (39·5% uranium-lead plus 60·5% thorium-lead).

\* Privately communicated.

The ages can now be calculated separately from each type of lead :—

No. 2.—

$$\left. \begin{array}{l} \frac{\text{Uranium-lead}}{\text{U}} \times 6,600 = 0.076 \times 6,600 = 502 \text{ m.y.} \\ \frac{\text{Thorium-lead}}{\text{Th}} \times 18,000 = 0.026 \times 18,000 = 468 \text{ m.y.} \end{array} \right\}$$

No. 7.—

$$\left. \begin{array}{l} \frac{\text{Uranium-lead}}{\text{U}} \times 6,600 = 0.083 \times 6,600 = 548 \text{ m.y.} \\ \frac{\text{Thorium-lead}}{\text{Th}} \times 18,000 = 0.023 \times 18,000 = 414 \text{ m.y.} \end{array} \right\}$$

No. 10.—

$$\left. \begin{array}{l} \frac{\text{Uranium-lead}}{\text{U}} \times 6,600 = 0.078 \times 6,600 = 515 \text{ m.y.} \\ \frac{\text{Thorium-lead}}{\text{Th}} \times 18,000 = 0.021 \times 18,000 = 378 \text{ m.y.} \end{array} \right\}$$

In each case the age calculated for the uranium-lead is somewhat higher than that calculated from the thorium-lead, but the results are definitely incompatible with Joly's claim that lead-uranium ratios may give results that are four times too high\*. Joly bases this claim on a comparison of the ratio 0.066 given by pitchblende No. 19 with the ratio 0.017 given by thorite No. 17. But thorite No. 18 gives the ratio 0.065, and contains even less uranium relative to thorium than No. 17. There is clearly no reason whatsoever for picking out No. 17 as being correct while rejecting No. 18 as incorrect. Indeed, were it not for Honigsmid's exceptionally careful work, it would be difficult to resist the straightforward conclusion that the true ratio is of the order 0.066. It is possible that Joly based his age estimate on No. 17 alone, on account of the fact that Soddy determined the atomic weight of the lead separated from that particular thorite. Soddy obtained the value 207.74, and from the same material Honigsmid obtained 207.77, this being the mean value of three determinations. From the average of these results the uranium-lead is found to be 12 per cent. of the total lead, and the thorium-lead 88 per cent. of the

\* 'The Surface History of the Earth,' 1925, p. 153.

total lead. The ages calculated separately are :—

No. 17.—

$$\left. \begin{array}{l} \frac{\text{Uranium-lead}}{\text{U}} \times 6,600 = 0.026 \times 6,600 = 173 \text{ m.y.} \\ \frac{\text{Thorium-lead}}{\text{Th}} \times 18,000 = 0.006 \times 18,000 = 101 \text{ m.y.} \end{array} \right\}$$

These results again disprove the contention that the uranium-lead ratio may be four times too high. What they do suggest is that lead has been leached out of the mineral (since the amount of lead now left is relatively so low), and that thorium-lead has now been removed to a greater extent than uranium-lead. The analysis of Honigschmid's results points to the same conclusion, as indeed do all the results of Table II.

On this hypothesis, which will be further discussed in a later section of this paper, the most nearly correct ratio for age-determination would be 0.083, obtained from the uranium-lead of thorianite No. 7. The thorium pegmatites of Ceylon would then be of the same age as the uraninite pegmatites of Katanga (lead-ratio 0.084) and the pegmatites of Brazil\* (lead-ratio 0.084).

The Ceylon results still leave room for the possibility that uranium may have disintegrated more rapidly in former ages; but they also show that it has certainly not disintegrated four times as rapidly, and that the correction due to such possible variation, if any, is very small. This conclusion follows from the analysis of Nos. 2, 7, 10, and 17, and from the fact that many of the thorium minerals give ratios as high or higher than the pitchblende. The variability of the ratios must be almost wholly a consequence of irregular leaching.

TABLE III.—The pegmatites of the Arendal District which provide this suite of minerals are of Middle Pre-Cambrian age. Here, as in the other series, the data show that the lead-ratios do not depend on the relative richness in uranium. One of the thorites and one of the monazites give ratios of the same order as three of the uranium minerals. The thorium minerals, however, display a far greater variation among themselves than do the uranium minerals, and are clearly not reliable as indices of age.

\* From a new analysis by E. P. Henderson, privately communicated by Prof. A. C. Lane



TABLE III.—Thorium and Uranium Minerals of Middle Pre-Cambrian Age from the neighbourhood of Arendal, Norway.

Ref.	Mineral.	U.	Th.	Pb.	Th/U.	Pb/(U+0.37 Th).
1.	Uraninite.	55.05	3.22	9.78	0.06	0.172
2.	Uraninite.	61.27	3.65	10.16	0.06	0.162
3.	Cleveite.	54.0	4.05	10.16	0.08	0.183
4.	Nivenite.	56.25	6.66	9.40	0.12	0.160
5.	Xenotime.	2.88	2.14	0.62	0.75	0.168
6.	Uranothorite.	8.80	45.50	1.55	5.2	0.160
7.	Orangite.	8.10	46.40	1.2	5.7	0.049
8.	Monazite.	—	6.28	0.30	—	0.129
9.	Monazite.	—	8.45	0.53	—	0.166
10.	Monazite.	—	10.18	0.24	—	0.063

- 1, 2. Analyses by Hillebrand: U.S. G. S. Bull. 2:0, 1903, p. 114.
- 3, 4. Analyses by Hidden & Mackintosh: Hintze, *Mineralogie*, i. p. 1675.
5. Analysis by Blomstrand: *G. För. Föhr.* ix. p. 185 (1887).
6. Analysis by Lindstrom: Hintze, *Mineralogie*, i. p. 1675.
7. Analysis by Hidden: *Am. J. Sci.* xli. p. 440 (1891).
- 8, 9, 10. Dana's 'Mineralogy,' 6th ed. p. 751.

It will be noticed that uraninite No. 1 gives a higher lead-ratio than No. 2, of which it is an altered variety. Cleveite, No. 3, is also an altered form of uraninite, and gives a still higher ratio. The analyses show that in the course of the alteration there is a loss of uranium, but, proportionately to the uranium, an actual gain in lead. This indicates that the lead in uraninites is present in a form that resists removal by leaching. Some of the thorium minerals, on the contrary, have lost lead, and therefore, if the percolating solutions responsible for the alterations have introduced lead into the altered uraninites, the added lead should be largely thorium-lead.

Fortunately it is possible to test this deduction by analysing the results for Cleveite, No. 3. Lead from this mineral was supplied by Mlle. Ellen Gleditsch to Messrs. Richard and Wadsworth, who determined its atomic weight as 206.084. The lead from cleveite therefore consists of 4.2 per cent. of thorium-lead and 95.8 per cent. of uranium-lead. Applying these proportions to the chemical analysis

of the mineral itself, we get :—

No. 3—

$$\left. \begin{array}{l} \frac{\text{Uranium-lead}}{\text{U}} \times 6,600 = 0.18 \times 6,600 = 1,188 \text{ m.y.} \\ \frac{\text{Thorium-lead}}{\text{Th}} \times 18,000 = 0.106 \times 18,000 = 1,908 \text{ m.y.} \end{array} \right\}$$

Evidently the lead introduced must have been rich in thorium-lead, and this could only have come from thorium minerals undergoing leaching. In Table III. we have therefore definite evidence that the lead in thorium minerals is removed more readily than the lead in uranium minerals. Further, when lead is introduced into a uraninite undergoing alteration, it tends to be in part fixed there, presumably by the formation of a highly insoluble compound.

TABLE IV.—Thorium and Uranium Minerals of Pre-Cambrian Age from Llano Co., Texas.

Ref.	Mineral.	U.	Th.	Pb.	Pb/(U+0.37 Th.)
1.	Uraninite.	55.18	5.90	9.35	0.163
2.	Uraninite.	56.45	6.66	9.43	0.160
3.	Mackintoshite.	19.75	39.86	3.47	0.100
4.	Thorogummite.	19.70	31.40	2.01	0.064
5.	Yarrialite.	2.28	7.70	0.45	0.089

1. Hillebrand : Am. Journ. Sci. xlii. p. 391 (1891).
2. Mackintosh : Am. Journ. Sci. xxxviii. p. 481 (1889).
- 3, 4. Hillebrand : Am. Journ. Sci. xlv. p. 101 (1893).
5. Hillebrand : Am. Journ. Sci. xiii. p. 149 (1902).

TABLE IV.—The minerals from Llano County, in Texas, are from pegmatites of Pre-Cambrian age, the associated granites being similar in general character to the Lorrian or Algonian granites \*. With the exception of the uraninites, most of the minerals are far from fresh, and they are therefore of little value for age-determinations. Becker used them, or rather misused them, to cast doubt on the validity of the whole method of measuring geological time by lead-ratios. Barrell, however, in the paper cited \*, has given a careful account of the evidence relating to the Llano minerals, and has pointed out that the uraninites give the same lead-ratios as Middle Pre-Cambrian minerals from Canada, Norway, Sweden, and Africa. To these localities

\* J. Barrell, Bull. Geol. Soc. Am. xxviii. p. 862 (1917).

Ceylon may also be added. All give ratios of about 0.16 and together they provide a most valuable datum line for the correlation of Pre-Cambrian formations in widely separated lands.

The three thorium minerals (Nos. 3, 4, and 5) are inserted to show, as before, the tendency to loss of lead. Although no atomic-weight determinations have been made, direct mineralogical evidence is available showing the effects of alteration due to percolating waters. Thorogummite No. 4 is a yellowish brown residual mineral produced from mackintoshite No. 3 by oxidation and further hydration. Corresponding to this change, the lead-ratio is lower than that of mackintoshite, which in turn gives a lower ratio than the uraninites. Thus there is clear evidence that the thorium minerals have suffered a loss of lead just as was deduced in the case of those from other localities. The uraninites, on the contrary, are abnormal neither in oxidation nor hydration, showing that the ratios derived from them are not likely to have been vitiated by external interference.

*The Loss of Lead from Thorium Minerals.*

In every case for which data are available, thorium minerals, without exception, seem to have lost part of the lead that had accumulated in them, and, moreover, to have lost thorium-lead in greater proportion than uranium-lead.

Whenever atomic-weight determinations have made it possible to calculate the proportions of the two isotopes, the preferential abstraction of thorium-lead is clearly indicated:—

Table and No.	Mineral.	Age from Thorium-lead	Age from Uranium-lead.	Difference.
I, 9 ...	Thorite, Brevik.	198 m.y.	257 m.y.	30 percent.
II, 2 ...	Thorianite, Ceylon.	468	502	7 .. ..
II, 7 ...	" "	414	548	32 .. ..
II, 10 ...	" "	378	515	36 .. ..
II, 17 ...	Thorite, "	108	173	60 .. ..

Had the Ceylon minerals not been interfered with by external agencies, then all the ages calculated in each way should have agreed, and should have been the same as those calculated from the ratio  $Pb/(U+0.37\ Th)$ . It is impossible to explain the discrepancies either by assuming that the atomic weights of thorium-lead and uranium-lead depart slightly from the integral values (as quite probably they do), or by assuming slightly different values for the

half-periods of uranium and thorium. The possible presence of ordinary lead has also been considered, but that assumption equally fails to explain the anomalies, and is in any case unjustified by the mineralogical evidence. Galena does not occur in association with any of the minerals under discussion. Galena does occur with the pitchblende of certain mineral veins, but in pegmatites it is extremely rare.

Both uranium-lead and thorium-lead have chemical properties that are identical with those of ordinary (207·2) lead, and it may seem incredible that one should be removed from a mineral in greater relative amount than the other. There remains, therefore, the further possibility that both isotopes of lead have been leached out in the same proportion as that in which they were generated, but that uranium has disintegrated progressively more rapidly in the past. On this assumption the ages of the Ceylon minerals calculated from uranium-lead should be higher than those calculated from thorium-lead, and higher by the same percentage throughout the series. Reference to the above figures shows that the actual percentages vary from 7 to 60 per cent. The average percentage is 34 per cent., practically the same as that for the Brevik thorite (which is only half the age), instead of being more than twice as high, as it should be on the assumption made.

Clearly the hypothesis that thorium-lead is preferentially leached out is the only one that seems to provide an explanation.

Analyses of primary uranium minerals, on the other hand, rarely reveal any loss of lead; and when they are altered by natural waters, the tendency is for lead, on balance, to be gained either absolutely or relatively to the uranium that is left. Table III. has already afforded excellent examples of this rule. Another case has been recorded recently by Ellsworth, who has carefully analysed uraninites from the Middle Pre-Cambrian pegmatites of Ontario. An externally altered specimen gave a ratio of 0·171 against an average ratio of 0·15 from five specimens not externally altered\*. An altered uraninite of North Carolina gave a ratio of 0·053, whereas carefully selected material gave 0·049. An altered pitchblende from Gaya, India, gave nearly 0·2, while a fresh specimen gave 0·13.

This rule cannot, of course, be expected to hold when, as at Katanga, uranium minerals have been completely dissolved by ascending solutions and new secondary minerals deposited elsewhere, nor does it seem to apply to the

\* H. V. Ellsworth; *Am. Journ. Sci.* ix. p. 143 (1925).

pitchblende of Ceylon, of which, however, more analyses would be welcome. Uniformity of behaviour under the attack of altering processes is naturally not to be anticipated, and the fact that in so many cases altered uranium minerals do show an increase of lead is therefore the more significant.

It follows from the above considerations that in minerals the lead formed from uranium should exist in a relatively insoluble compound, and that the lead generated by thorium should exist in a more soluble compound. Now, when an atom of lead comes into existence in the crystal lattice of uraninite, it must be surrounded by atoms of uranium and oxygen; that is to say, it is in an acidic environment. Helium, being inert, need not be considered. It seems probable, therefore, that the general association of atoms should correspond to the assemblage required to form a molecule of lead uranate. At first the arrangement of atoms would be haphazard, but if water passed slowly through the crystal, the resulting localized mobility and kinetic exchange would promote at each point the formation of the most insoluble compound possible; that is to say, lead uranate. Moreover, if lead were introduced into the crystal lattice by water, one would expect that an interchange of atoms would then be possible, some of the lead being left and some of the uranium being removed. In this way the material left behind would become more insoluble than it was originally and the lead-uranium ratio would be increased.

In thorium minerals the lead could not form a thorate, as thorium and oxygen do not constitute an acidic environment, and corresponding with this no thorates are known to exist. In thorianite the lead should be largely present as an oxide; and in thorite partly as oxide, and partly perhaps as a silicate. In both minerals the most probable lead compounds are therefore of a comparatively soluble type.

In mixed minerals, such as thorianites rich in uranium, the tendency to loss of lead should be less than in thorites poor in uranium, as we find to be the case. This follows from the fact that the thorium-lead migrating out of a thorianite must pass through an assemblage of atoms many of which are uranium and oxygen. Part of the lead which would otherwise escape should thus be arrested and fixed as lead uranate. In thorites the corresponding capacity to retain lead is practically negligible.

The hypothesis of preferential leaching is thus in accordance with chemical probabilities, and for the first time the

long-puzzling discrepancies between thorium and uranium minerals appear to receive an adequate explanation.

*Pleochroic Haloes.*

In the course of his remarkable researches on pleochroic haloes, Joly \* found that the uranium halo has a greater radius in micas from older granites than in those from younger rocks. The final results of his carefully confirmed measurements are these :—

Source of Mica.	Radius of Halo in mm.	Geological Age.
Mourne Mts., Ireland .....	0·0136	Tertiary.
Ballyellen, Ireland .....	0·0146	Devonian.
Rapakivi, Finland .....	0·0152	Late Pre-Cambrian.
Arendal, Norway .....	0·0155	Middle Pre-Cambrian.
Ytterby, Sweden .....	0·0160	

Since there is a definite relation between the rate of disintegration of an atom and the range of the  $\alpha$ -particles it emits, Joly considers it probable that uranium or some part of it decayed more rapidly in the past than it does now, and that the rate, and consequently the radius of the resulting haloes, has gradually decreased through geological time. Thorium haloes reveal no variation of radius with age, and this points to some unique complication in the uranium series that is not shared by the thorium series. Further, it proves in the only way yet possible that the rate of disintegration of thorium has not varied during geological time. An alternative explanation of the uranium anomaly would thus clear the way towards using uranium haloes as evidence that the rate of disintegration of uranium has also been uniform, or practically uniform.

Several alternative explanations of the halo variations are possible. Some of these (such, for example, as depend on temperature changes in the rocks, long-range  $\alpha$ -particles from the emitting centre, and direct collisions between  $\alpha$ -particles and other elements) would require similar variations in thorium haloes, and therefore need not be considered.

I am indebted to my friend Dr. R. W. Lawson for directing my attention to the probable bearing of the actinium series on the problem. Uranium differs from thorium in giving rise to two distinct series of daughter

\* Proc. Roy. Soc. A, cii. p. 682 (1923).

elements, one of them proceeding by way of radium (97 per cent.) and the other by way of actinium (3 per cent.). That the relation of actinium to uranium is a genetic one is established by the constancy of the ratio  $\text{Ac/U}$  in minerals.

A. S. Russell has given reasons\*, based on empirical relations, for concluding that actinium arises from an isotope of uranium having an atomic weight of 239. He calculates the half-period of this hypothetical actino-uranium as about  $8 \times 10^9$  years. If this be approximately correct, then in the past the relative abundance of actino-uranium must have been progressively higher. However, no one claims that the oldest haloes investigated by Joly are older than about  $10^9$  years, and consequently, within that period, the percentage of actino-uranium cannot reasonably be placed higher than 4 or 5 per cent. of the total uranium.

Such an isotope of uranium, or one of its daughter elements, would probably emit  $\alpha$ -particles having the range required to explain the older haloes. As the percentage of actino-uranium would be small, the haloes due to it, or to its family, could not be visibly developed until after a geologically long period of time. In young haloes the effects of the actinium series would not be detectable at all. The actino-uranium halo, for example, would take at least twenty times as long to develop as the uranium halo. Moreover, once the subsidiary halo had reached the radius corresponding to the peak of the ionization curve, it would still tend to grow slowly outwards by the small amount corresponding to the last and less effective part of the range. The apparent radii of "uranium" haloes would therefore increase from younger to older examples, the later stages of growth taking place more slowly than the earlier. This deduction matches the actual data, as reference to the table on p. 1069 shows, for the time-interval between the Arndal and Rapakivi granites is roughly twice as long as that between the younger Irish granites.

If the above explanation be correct in principle, then the higher lead-uranium ratios would certainly be slightly too high, but not by more than 1 to 3 per cent. This conclusion is consistent with the atomic-weight determinations on lead from uranium minerals. The atomic weight of uranium-lead cannot be far from 206, and, according to Russell's interpretation of the actinium series, that of actinium-lead should be 207. Assuming integral atomic weights, then the mixed lead in minerals should be 206.04 or

\* Phil. Mag. xlv. p. 642 (Oct. 1923).

206.05 according as 4 or 5 per cent. of actinium-lead is present. The lowest value yet found is 206.046 for lead from the uraninite of Morogoro, Tanganyika Territory\*. Lead from the Katanga uraninite has an atomic weight of 206.048 (and the mineral is free from thorium), and that from Bröggerite, Moss, Norway, with which a trace of thorium-lead must be associated, has an atomic weight of 206.06. These results show that if actinium comes from an undetected isotope of uranium, then the lead derived from it must have accumulated at practically the same rate as that followed to-day. Otherwise the atomic weights would be higher than they are. Even if in Middle Pre-Cambrian times the hypothetical isotope had been twice as abundant as it could be now, and the results do not admit so much as possible, then the age correction to be made would be a reduction of only 3 per cent. This would have to be slightly reduced to take into consideration the fact that uranium itself was more abundant then than now.

On the other hand, Joly's deduction that the larger lead-uranium ratios may be four times too high involves the assumption that at least 75 per cent. of the lead in any Pre-Cambrian mineral had been derived from an isotope that has now almost disappeared. Judging from all experience, this hypothetical isotope would have an atomic weight different from that of uranium as we know it, and therefore the atomic weights of the resultant lead in minerals should be expected to differ far more from 206 than they actually do.

Apart from Russell's views, it is at present generally considered likely that actinium arises from uranium II. This element disintegrates dually, 97 per cent. changing into ionium, the parent of radium, and 3 per cent. changing to uranium Y, which is thought to change to proto-actinium, the parent of actinium. In this case the apparent variation in the radii of the uranium haloes might be due to the cumulative effect of the  $\alpha$ -activity of proto-actinium. Actinium itself is a  $\beta$ -ray emitter and does not generate a halo. As before, the effect superimposed on the normal uranium halo would become progressively visible to the maximum radius only after a very long period, the equilibrium amount of the emitting element being derived from only 3 per cent. of the original uranium. It is noteworthy that in the main or radium branch, ionium gives a halo of nearly the same radius as that of the alleged uranium halo of Ytterby mica.

This explanation, like that based on Russell's actino-uranium, is almost equally consistent with atomic-weight

\* O. Honigschmid and St. Horovitz: *Wien. Anz.* 15th Oct., 1914.



evidence, and it requires no correction to lead-ratios since no isotope of uranium is implied.

It must finally be pointed out that the ranges of  $\alpha$ -particles from uranium are not yet exactly known. The recent work of Gudden is itself based on uranium haloes in fluspar, and cannot therefore be used as providing independent evidence\*. No direct measurements have yet been made, and until that difficult task has been achieved, only intelligent speculation is possible based on empirical relations and guided by atomic-weight evidence.

Summing up, it is clear that the isotopic constitution of what we call uranium is not yet adequately known. The variable radii of uranium haloes can be explained in more ways than one. While Joly's deduction from that variation seems to be out of harmony with the ascertained atomic weights, those advanced here by Lawson and myself are consistent with them. In no explanation is it yet possible to appeal to the actual ranges of the  $\alpha$ -particles from uranium, because these have not been directly observed.

Pleochroic haloes should therefore not be used to throw doubt on the validity of the lead-ratios, or to suggest a wide departure from a uniform rate of disintegration in the case of uranium. It is worth noticing, however, that Joly's measurements may afford a basis for a new method for determining within broad limits the ages of granites containing micas with haloes. By plotting time against halo-radii a scale is given by reference to which the ages of other measured haloes could be roughly estimated. The method requires extraordinarily careful measurements, and is therefore not to be lightly undertaken.

#### *Cycles of Basaltic Fusion and Consolidation.*

In a recent paper in the 'Geological Magazine' (Dec. 1925) I attempted to show that the surface history of the earth points to the interweaving of at least two different cycles of fusion and consolidation, one in the basaltic layer, and the other (with a much longer period) in an underlying layer assumed to be composed of peridotite or its chemical equivalent. This extension of Joly's brilliant conception is also in agreement with the longer estimates of geological time. Nevertheless, I consider that far-reaching hypotheses of this kind should not be regarded as providing any sort of method for estimating geological time, but should themselves be tested, and modified where necessary, by reference to the ascertained data of geological time-measurements.

\* *Zeit. Physik*, xlv. p. 110 (1924).

*Conclusions.*

A careful study of the evidence on which certain measurements of geological time have been based is consistently in favour of the longer estimates.

1. The sodium method fails for lack of reliable data and lack of adequate knowledge of the geo-chemical cycle of sodium salts (and particularly of sodium chloride in ground-waters) in geological processes.

2. Thorium-rich minerals give lead-ratios that vary from those of uranium minerals of the same geological age down to very low values. There is no reason why the lowest ratio should be regarded as the most reliable index to age. All are suspect, and none of them has much more value than a helium-ratio, which admittedly gives a minimum result. If uranium disintegrated more rapidly in the past, then there should be a relation between the lead-ratios and the ratio of thorium to uranium. The actual variation is quite irregular. Some thorium minerals give the same ratios as uranium minerals, and therefore there is no evidence that the uranium ratios are appreciably too high.

3. It is suggested that the discrepancies in thorium minerals are due to the fact that lead present as oxide or silicate would be more easily removed by percolating waters and kinetic exchange than the lead in uranium minerals, which may be present actually or potentially as a highly insoluble uranate.

4. Pleochroic haloes due to uranium provide no evidence that uranium has disintegrated more rapidly in the past, as Joly has contended. Other explanations are shown to be more probable as tested by atomic-weight evidence. One conjecture involves the possibility that a hypothetical actino-uranium of shorter life than uranium was formerly slightly more abundant than now. The reduction in the time estimates that would be necessary if this explanation were proved correct would range only between 1 and 3 per cent., not up to 300 per cent. as has been suggested.

5. Atomic-weight determinations on lead from uranium minerals support the view that uranium has always disintegrated at substantially the same rate as at present. At the worst, if the rate has varied it cannot have decreased (by the wearing-out of an isotope) by more than about 3 per cent. since Middle Pre-Cambrian times.

6. Finally, as a general deduction, we may safely assert that the evidence presented shows that the age of a fresh primary mineral free from ordinary lead is given to the

right order by the formula  $\frac{\text{Pb}}{\text{U} + 0.37 \text{Th}} \times 6,600$  million years.

The factor 0.37 may later be found to be 0.35 or 0.38. The factor 6,600 may be 6,200 or 7,000\*. A reduction varying up to 3 per cent. is necessary in all cases to take into consideration the obvious fact that the amounts of thorium and uranium now in a mineral must be less than those present when the mineral crystallized. A further reduction of 1 to 3 per cent. may in the future be found necessary if the parent of actinium should be identified with an isotope of uranium for which the name actino-uranium has already been proposed. Taking the outside limits of all combinations of the possible variables, the length of time that has elapsed since the crystallization of the Middle Pre-Cambrian pegmatites of Norway, Sweden, Ontario, Texas, and Africa is found to be between 930 and 1,080 million years, with 1,020 million years as the most probable value on present data. Higher ratios for the Lower Pre-Cambrian are known, but cannot yet be regarded as so well established as those for the Middle Pre-Cambrian.

It is my privilege, in conclusion, to express my thanks to Dr. R. W. Lawson, Professor Irvine Masson, and Dr. J. A. Smythe for their active interest in the problems of this paper; for discussing with me various points on which I sought their advice; and for their salutary criticisms and helpful suggestions.

XCVII. *Variation of Logarithmic Decrement with Amplitude and Viscosity of Metals.*—III. By G. SUBRAHMANIAM, M.A., A.Inst.P.†

THIS is the third of a series of investigations which the author has undertaken in connexion with the variation of logarithmic decrement with amplitude and viscosity of metals. On the present occasion the study is extended to nine more metals, namely: gold, silver, platinum, tungsten, nickel, lead, tin, platinoid and phosphor bronze. Wires of gold, silver, lead and tin are made locally from very pure specimens of these metals, taking all possible precautions against their being "hollow drawn." Since gold, lead and tin in such pure forms are very soft and are easily deformed,

\* Ellsworth gives this factor as 7,900 in an important paper on the Ontario uraninites and the subject generally (Am. Journ. Sci. p 133, Feb. 1925). The figure he adopts is quoted from an early paper by Lawson, and is based on old data which were faulty in regard to the half-period of radium.

† Communicated by Prof. A. L. Narayan.

these wires are kept straight and not wound on bobbins. The platinum wire is supplied by Smith & Co., of Madras, and is of guaranteed purity. The remaining wires—tungsten, nickel, platinoid and phosphor bronze are procured for us by Baird & Tatlock, of London, and are of good commercial quality, but not of absolute purity.

The method of experiment and the preliminary treatment to which each of the test wires is subject before it is finally taken to the vacuum chamber, are set forth in detail in my first communication \*. I have, however, encountered certain difficulties with the soft metals—gold, lead, and tin—which have necessitated some modifications. In an attempt to keep each of them stretched by attaching a weight at the lower end these metals are found to “flow” perceptibly. Even a small weight long enough applied seemed sufficient to produce an appreciable effect, as, for instance, when the wires are kept loaded overnight. In these cases it is, therefore, found necessary to use moment of inertia bars of comparatively smaller masses, consisting essentially of two cylindrical brass pieces of equal mass and dimensions, fixed at the ends of a horizontal cross-piece, at equal distances from the axis of rotation. The bar used with the gold wire weighed about 124 grm., while that used with lead and tin wires only 38 grm. The moments of inertia of these two bars are determined experimentally by the usual method, and are found to be 1522 and 406.4 grm. cm.<sup>2</sup> respectively.

With regard to lead and tin wires the zero, in addition, is found to be most erratic. The method of finding the logarithmic decrement under such conditions of unsteady zero affords an interesting illustration of the following theory of damped vibrations, suggested by Rowell †; but his assumption that  $A_0$  is constant is by no means justifiable. We have, using Rowell’s notation, the equation of motion in such cases :

$$m\ddot{x} + k\dot{x} + c^2x \pm F = 0,$$

indicating that the system oscillates alternately about two origins distant  $\frac{2F}{c^2}$  apart.

The solution of the above equation is evidently

$$x = \mp \frac{F}{c^2} - A_r e^{-\frac{kt}{2m}} \cos(n_1 t + \epsilon),$$

where

$$n_1 = \sqrt{\frac{c^2}{m} - \frac{k^2}{4m^2}}.$$

\* Phil. Mag. April 1925.

† Phil. Mag. July 1922, pp. 284-5; Nov. 1922, pp. 951-3.

In the above equation the sign of  $\frac{F}{c^2}$  depends on  $(-1)^r$  for the  $r$ th semi-oscillation. Hence

$$x = (-1)^r \frac{F}{c^2} - A_r' e^{-\frac{kt}{2m}} \cos(n_1 t + \epsilon).$$

Put

$$A_r' = A_r e^{-\frac{k}{2m} \cdot \frac{\alpha}{n_1}} \sec \alpha \cdot d^r (-1)^r,$$

where

$$\cos \alpha = \frac{n_1}{\sqrt{\frac{k^2}{4m^2} + n_1^2}} \quad \text{and} \quad d = e^{-\frac{k}{2m} \cdot \frac{\pi}{n_1}},$$

the latter being obviously the decrement.

Also put  $\frac{F}{c^2} = s$ .

$$\begin{aligned} \frac{dx}{dt} &= A_r' e^{-\frac{kt}{2m}} \left\{ n_1 \sin(n_1 t + \epsilon) + \frac{k}{2m} \cos(n_1 t + \epsilon) \right\} \\ &= A_r' e^{-\frac{kt}{2m}} \left( \sqrt{\frac{k^2}{4m^2} + n_1^2} \right) \{ \cos \alpha \sin(n_1 t + \epsilon) \\ &\quad + \sin \alpha \cos(n_1 t + \epsilon) \} \\ &= A_r' e^{-\frac{kt}{2m}} \cdot \sqrt{\frac{k^2}{4m^2} + n_1^2} \cdot \sin(n_1 t + \epsilon + \alpha). \end{aligned}$$

We know  $\dot{x} = 0$  when  $n_1 t + \epsilon + \alpha = 0$ .

Let time be reckoned from  $\frac{\alpha}{n_1}$  sec. after starting,

so when  $t = -\frac{\alpha}{n_1}$ , we have  $\dot{x} = 0$ .

$\therefore -\alpha + \epsilon + \alpha = 0$ , thus making finally  $\epsilon = 0$ .

So end of the first semi-oscillation is at time  $\frac{\pi - \alpha}{n_1}$ .

Again, because velocity is zero at beginning of second semi-oscillation, i. e. at time  $\frac{\pi - \alpha}{n_1}$   $\therefore \epsilon = 0$ ,

similarly  $\epsilon = 0$  for the third semi-oscillation, and so on.

Generally  $\dot{x} = 0$  when  $n_1 t + \alpha = r\pi$ , i. e.  $t = \frac{r\pi - \alpha}{n_1}$ .



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Hence

$$x_r = (-1)^r s + \frac{2s(-1)^r}{d-1} - \left( A_0 + \frac{2s}{d-1} \right) \frac{1}{(-d)^r}$$

and

$$x_{r+2} = (-1)^{r+2} s + \frac{2s(-1)^{r+2}}{d-1} - \left( A_0 + \frac{2s}{d-1} \right) \frac{1}{(-d)^{r+2}}$$

$$\therefore x_{r+2} - x_r = \left( A_0 + \frac{2s}{d-1} \right) \left\{ \frac{1}{(-d)^r} - \frac{1}{(-d)^{r+2}} \right\}.$$

Similarly

$$x_{r+4} - x_{r+2} = \left( A_0 + \frac{2s}{d-1} \right) \left\{ \frac{1}{(-d)^{r+2}} - \frac{1}{(-d)^{r+4}} \right\}.$$

Finally

$$\frac{x_{r+2} - x_r}{x_{r+4} - x_{r+2}} = d^2.$$

Thus the decrement is found for lead and tin wires by noting three successive half-swings to the same side of zero.

### *Experimental Results.*

In all these experiments the scale is, as usual, held at a constant distance of 74 cm., so that an amplitude of one cm. corresponds to an angular twist of 0.39 of a degree. The maximum twist to which each of the test-wires is subject is about 5°, except in the case of gold, lead and tin, where it is much smaller.

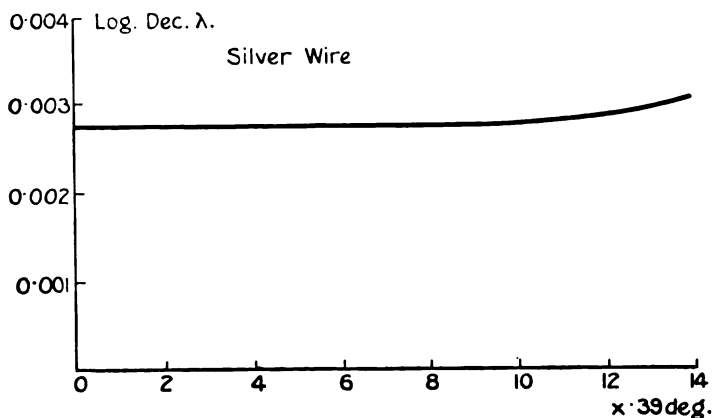
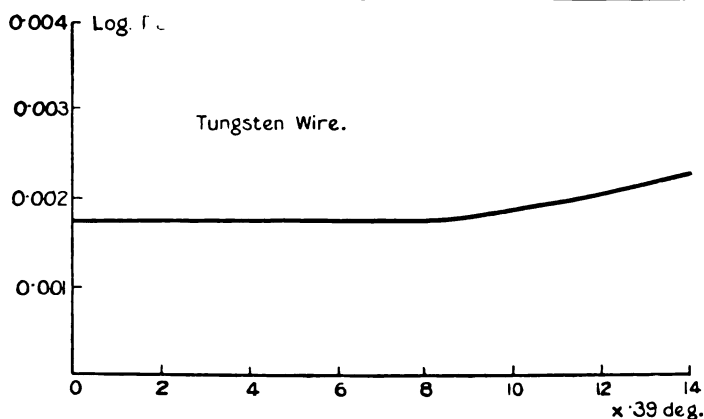
The experimental values are indicated in the accompanying graphs accurately. Tabular forms are, therefore, avoided from considerations of space. It will be seen from the graphs that the decrement-amplitude curves for tungsten, silver, platinoid and phosphor bronze wires run parallel to the  $x$ -axis until a limiting twist is reached, and thereafter increase, more or less linearly, with the amplitude, suggesting an equation of the form  $\lambda_a = \lambda_0 + f(a - m)$ , where the constants " $a$ " and " $m$ " are, of course, different for different materials. These limiting twists are found to be 2.36, 2.58, 4.16, and 3.36 min. per unit length respectively. On the other hand, curves for platinum, nickel, and gold rise proportionately with the amplitude, and are therefore represented by  $\lambda_a = \lambda_0 + f(a)$ . With regard to lead and tin wires no such detailed investigation is found practicable.

For purposes of calculation the log. dec. is extrapolated for zero amplitude, and the value substituted in the equation

$$\eta = \frac{8I\lambda_0}{\pi \cdot T \cdot R^4}.$$

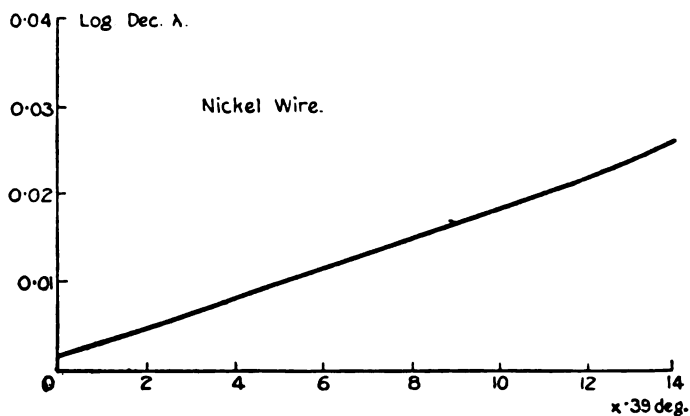
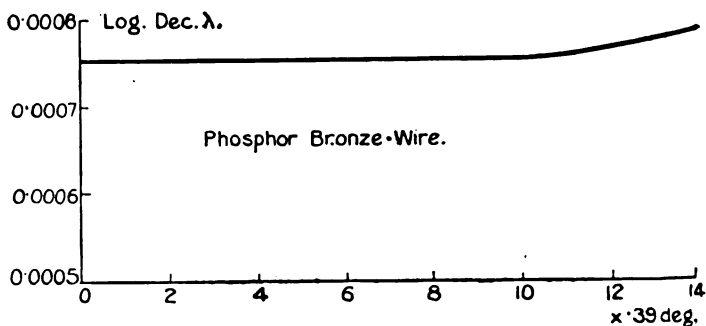
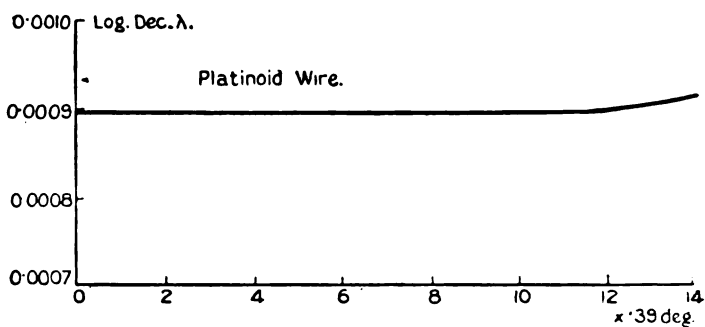
TABLE I.

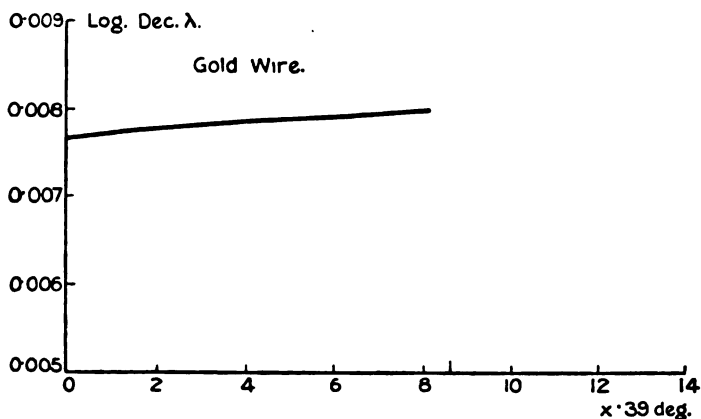
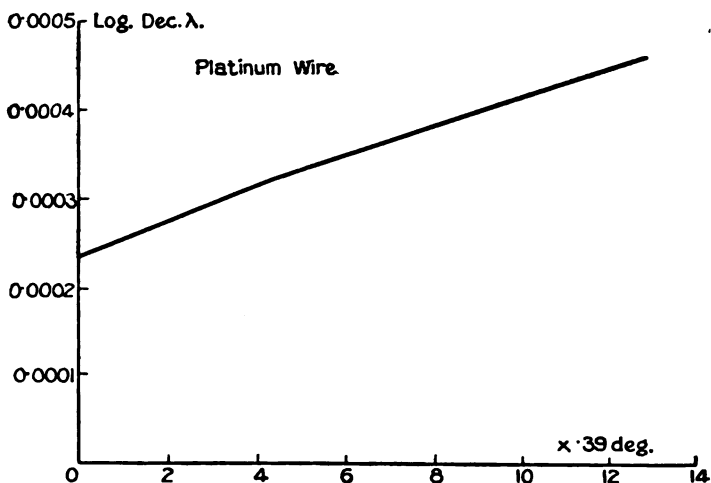
Metal.	I grm. cm <sup>2</sup> .	l cm.	R cm.	T sec.	$\lambda_0$	$\eta$ poises.
Tungsten ...	3563	71.4	.02525	3.212	.001742	$8.638 \times 10^6$
Silver .....	"	63.6	.02740	5.950	.002743	4.719 "
Platinoid ...	"	65.8	.03025	3.367	.0008978	1.901 "
Phosphor bronze. }	"	71.0	.02525	5.997	.0007519	1.986 "
Nickel .....	"	69.8	.02550	4.385	.001846	6.306 "
Platinum ...	3840.9	40.7	.01475	11.730	.0002381	1.707 "
Gold .....	1522	50.5	.02188	5.559	.007673	11.79 "
Lead .....	406.4	72.75	.03132	3.210	.06720	16.39 "
Tin.....	"	71.55	.02525	3.630	.07124	35.72 "





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The author, in conclusion, wishes to thank Prof. A. L. Narayan, M.A., D.Sc., F.Inst.P., for his stimulating interest in these investigations, and Prof. S. Purushotham, M.A., for valuable suggestions.

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XCVIII. *The Time of Excitation of Hydrogen Atoms.*  
*By J. S. McPETRIE, B.Sc., Aberdeen University\*.*

SUMMARY.

PREVIOUS workers on the light-emission from a beam of positive rays have assumed that the time during which an electron remains in an excited orbit is negligible, and their aim has been the determination of the time of emission. The present paper has for its object the determination of this time of excitation, and it is shown to be comparable with the time of emission.

One method used gives the value of about  $10^{-8}$  sec. for the time of excitation of the  $H_\beta$  line of the Balmer Series of Hydrogen.

A slightly different method is described for the determination of the values of both the times of emission and excitation. They are found to be approximately  $2 \times 10^{-8}$  sec. and  $7.5 \times 10^{-9}$  sec. respectively.

The slightly different results obtained for the time of excitation by the two methods are discussed, and reasons given for the small discrepancy.

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ON Bohr's Theory of Spectra an atom radiates energy when one of its extra-nuclear electrons returns from an unstable orbit to one of less energy, the frequency of the line emitted being given by the familiar equation

$$h\nu = E_1 - E_0,$$

where  $E_0$  and  $E_1$  is the energy-content of the atom when the electron responsible for the radiation is in the stable and unstable orbit respectively.

Wien in a number of papers (*Ann. d. Phys.*, 1919–1925) describes extensive research on the light given out by the moving atoms in a beam of positive rays. Using a spectrograph of large dispersion, he has measured the intensity of light-emission at various distances behind the cathode at different pressures and velocities. In his latest paper† he measures the variation of intensity at a point a short distance from the cathode at low velocities and high pressures. On the assumption of a definite time of excitation (*Verweilzeit*) he shows mathematically that it cannot be distinguished by this method from the actual

\* Communicated by Prof. G. P. Thomson, M.A.

† *Ann. d. Phys.* lxxvi. (Jan. 1925).

time of emission (Abklingkeit) due to the symmetry of the equation. The expression for the intensity also seems to indicate that, as the pressure in the positive-ray tube is increased, the intensity at any fixed point in the positive beam should first increase and then diminish, the rate of decrease of the intensity and the pressure required for maximum intensity being governed by the relative values of the time of emission and the time of excitation. His experiments indicate no such diminution of intensity, and he concludes that there is no time of excitation distinct from the actual time of emission.

Dempster \* has also worked on the measurement of the intensity of the light-emission from a beam of positive rays. He fired fast-moving positive rays into an evacuated observation space. As the pressure in this chamber decreased, the length of the visible beam of rays diminished to an approximately constant value. On measuring the velocity of the rays by the Doppler Effect, he found that this distance of visibility corresponded to a time of about  $5 \times 10^{-8}$  sec. This time represents the sum of the times of emission and excitation.

It will be seen by the above that the time of excitation has never been measured by any method without the intervention of the time of emission. The present paper describes an experiment made to determine whether there was a time of excitation and, if so, to measure its approximate value without having to consider the time of emission.

Consider a point A in the positive-ray beam. Suppose by means of a magnetic field we get rid of the atoms charged at A before reaching B not much further along the tube than A. The intensity of the light emission at B will be reduced due to the removal of the atoms which were charged at A, and which would have been emitting at B had it not been for their deflexion by the magnetic field. The magnetic field affects only the moving charged atoms at A. In the positive-ray beam, however, we have stationary and moving charged atoms and molecules. Stationary emitting atoms and molecules serve only to complicate matters enormously so their effect has to be nullified. This was done in the following experiments by studying the moved part of the  $H_{\beta}$  line of the Balmer Series of Hydrogen. This line Wien has shown is emitted by uncharged H atoms, and being also the most intense line in the positive-ray spectrum of  $H_2$ , suits our purpose admirably. It must thus be understood

\* Phys. Rev. Feb. 1920, and Astr. Journ. lvii. (May 1923).

that whenever intensity is mentioned below, it refers to that of the moved line only.

For the purpose of reducing experimental results it is convenient to consider two cases :—

- (a) High velocity positive rays.
- (b) Medium and slow velocity positive rays.

(a) If there is a time of excitation, a charged atom before it can emit has to capture an electron and pass through the excited state. The time for this to occur may be sufficient to cause an atom charged at A to pass beyond B, a short distance further on, before it can begin to emit, if the velocity of the atom be sufficiently large. In this case all atoms charged at A and gradually being neutralized between A and B would be beyond B before they get into the condition for emission. If we deflect these atoms charged at A, we make no difference to the intensity of the moved line at B, as none of the particles deflected would have been emitting at B even in the absence of the magnetic field. At smaller velocities, however, there would be a change in intensity at B, as some of the atoms charged at A would have time to regain an electron, pass through the excited state, and be in a condition for emission at B. This means that, as we increase the velocity of the rays, we come to a stage at which on switching on a magnetic field between A and B sufficiently intense to deflect all atoms charged at A into an earthed metal tube, we can detect no difference in the intensity of emission at B. This condition is satisfied if there is a time of excitation and the velocity of the rays is sufficient to cause all the atoms charged at A to pass beyond B in the excited condition. We have thus a method of determining absolutely the time of excitation (if any) of  $H_\beta$  without the necessity of taking into account the time of emission.

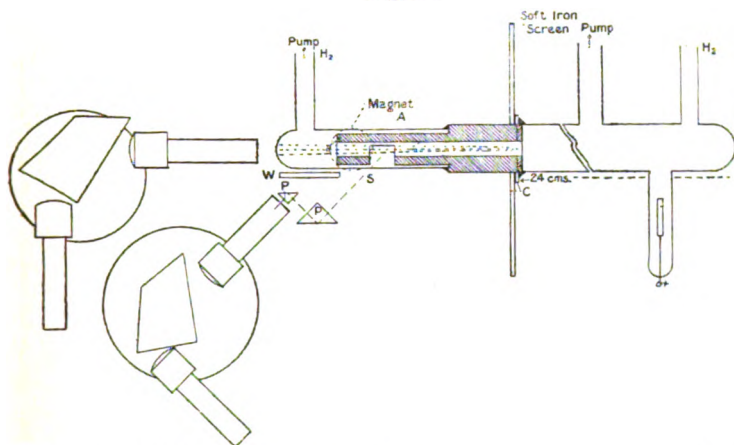
(b) In the general case of medium and slow velocity positive rays we can form an equation for the intensity at B with and without the magnetic field. This expression contains the times of emission and excitation as unknowns, the free paths in the charged condition being known from previous work by Ruchardt \*. On measuring the decrease in intensity at B, brought about at various velocities and pressures on excitation of the magnetic field, we can determine, approximately, the magnitude of these times

\* *Ann. d. Phys.* lxxi. p. 377 (1923).

separately, taking the value most nearly agreeing with that found in the case of the high-velocity rays as the time of excitation. Thus by using the result for the time of excitation found in (a), we can find the time of emission from the experiment made with medium velocity rays.

The apparatus consisted of a discharge-tube with an aluminium tube S 1.5 cm. long placed 7 cm. behind the cathode C in the path of the positive rays, the holes in S and C being parallel and each 0.5 cm. in diameter. The two chambers were thus at the same pressure, the large hole in the cathode being found necessary to obtain intensities sufficient for visual observation. A magnetic field could be excited transverse to the tube S by means

Fig. 1.



of a Du Bois magnet, MM, the strength of the field being sufficient to deflect all moving positive atoms in the beam into S, which was connected to C and to earth. A Hilger constant deviation spectrometer was placed to view the beam at B at an angle of about  $45^\circ$ . The prism P was arranged to reflect the light from A on to another reflecting prism covering the lower half of the slit of the spectrometer. Thus the image in the eyepiece of any line in the positive-ray spectrum of the gas in the discharge-tube consisted of two parts, the top half coming from A after two external reflexions and the bottom half from B viewed direct. In the mathematical expressions deduced below, it is the intensity of the moved line only that is considered; so a black screen was placed in the eyepiece

of the spectrometer to cut off the light from the long wave-length edge of the line under observation, the dispersion of the instrument not being great enough actually to separate the moving from the stationary line. An Ilford wedge-screen, W, could be passed in front of the top half of the slit of the spectrometer to reduce the intensity of the line seen in the eyepiece coming from B. This wedge was placed so as to make the two halves of the image in the eyepiece appear equally intense with no magnetic field across S when a reading of a scale attached to the wedge was taken. The magnet was then excited when the equality of intensity of the two halves of the image was destroyed, the top half being now brighter than the lower half. The wedge was therefore withdrawn until equality of intensity was again procured. A reading of the wedge-scale was again taken. The wedges used in the two methods of determining the time of excitation described in (a) and (b) above had different indices, so the shifts in the two cases do not correspond numerically. It will be seen that by observing A and B at the same time, we get over the difficulty of any change in the discharge-tube conditions brought about by any stray magnetic field. Both parts of image, even when the discharge-tube is well screened, are slightly diminished in intensity on switching on the magnetic field; but as it is the change in the relative intensity at A and B that is measured each time, the error due to this source is enormously decreased. A second Hilger spectrometer was placed to view the beam end-on in order to obtain a large reading for the Doppler effect. The pressure was also read. From these two measurements we can obtain the length of the free path of a positive atom, assuming it to be proportional to  $(\text{Velocity})^3/\text{Pressure}^*$ .

Table I. gives the measurements made with gradually increasing velocities.

The wedge-shift shown in the right-hand column of Table I. decreases with increasing velocity of the rays. This is shown in the accompanying graph (fig. 2), from which it will be seen that at a velocity of about  $1.5 \times 10^{-8}$  cm./sec. the shift of the wedge is too small to be detected. This means that the velocity of the atoms in the beam is sufficient to cause all atoms charged at A to travel a distance AB in the excited condition. The effect of the magnetic field, therefore, on the relative intensity of the beam at A and B is zero, as the atoms charged at A would not have

\* Ruchardt, *Ann. d. Phys.* lxxiii. p. 228 (1924).

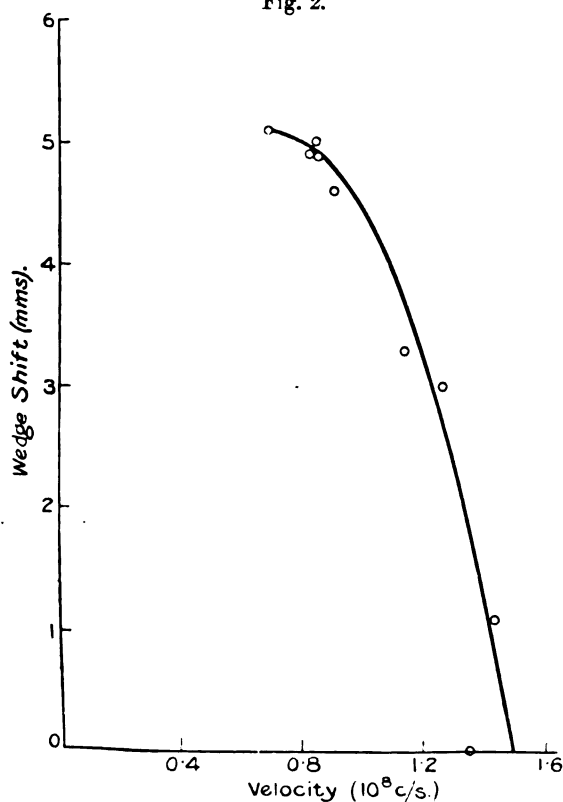
TABLE I.

Violet Edge. $H_{\beta}$	Velocity.	Wedge- shift.
4853.1	$6.7 \times 10^7$ c/s.	5.1 mms.
4850.6	$8.27 \times 10^7$ „	5.0 „
4850.6	$8.27 \times 10^7$ „	4.9 „
4851.7	$8.2 \times 10^7$ „	4.9 „
4849.5	$8.9 \times 10^7$ „	4.6 „
4845.35	$1.13 \times 10^8$ „	3.3 „
4843.6	$1.26 \times 10^8$ „	3.0 „
4840.7	$1.43 \times 10^8$ „	1.1 „
4842.0	$1.36 \times 10^8$ „	0.0 „

An actual set of readings is given below :—

Spark Gap .....	0.303 cm.
McLeod Gauge .....	0.0258 mm. Hg.
Doppler Effect.....	4850 : 4851 : 4851 : 4850.
Wedge-scale readings :.....	2.6-2.1 : 2.4-1.9 : 2.3-1.9 : 2.35-1.85 ; 2.4-2.0 : 2.38-1.9 : 2.38-1.88 : 2.4-1.88.
McLeod Gauge .....	0.0248 mm. Hg.

Fig. 2.





begun to emit at B in the absence of the magnetic field. The distance AB is equal to the length of the earthed tube S (and of the magnetic field), which was 1.5 cm.

Let T be the time of excitation. Then we have

$$T = d/V,$$

where  $d$  is the length of the tube S and  $V$  the velocity necessary for zero shift.

$$\therefore T = 1.5/1.5 \times 10^8 \\ = 10^{-8} \text{ sec.}$$

It should be noted that this method over-estimates slightly the time of excitation. This point, however, will be taken up in the discussion at the end.

We have now to consider the general case. Various expressions are obtained for the intensity of the light at the exit from the magnetic field corresponding to the different assumptions that are made as to the nature of the times of emission and excitation. In the following analysis it is assumed that all atoms remain in the excited condition for a definite time, and that the light emitted at  $x$  by a group of atoms  $N$ , all of which start to emit at  $x=0$ , can be represented by a function of the form  $KNe^{-bx}$ .

Let  $N$ ,  $N_1$ , and  $N_2$  be the concentration of charged, emitting, and excited moving atoms at the entrance to the field. Let  $L$  be the mean distance moved by a charged atom before being neutralized,  $l$  the mean distance of emission, and  $\lambda$  the distance through which an atom moves in the excited condition.

Number of charged atoms per c.c. at entrance to field is  $N$ .

Number still charged at  $\xi$

$$= N \left(1 - \frac{\xi}{L}\right) e^{-\frac{\xi}{L}},$$

where  $d$  is the length of the magnetic field and  $\left(1 - \frac{\xi}{L}\right)$  is a factor introduced so that at distance  $\xi$  equal to  $d$  there are no charged atoms.

Number losing charge in element  $\delta\xi$  at  $\xi$

$$= \frac{N}{L} \left(1 - \frac{\xi}{L}\right) e^{-\frac{\xi}{L}} \delta\xi.$$

\* Although the equations obtained are different, the arithmetical value of  $I_B/I_B$  found on substituting the various values for the time of emission does not vary much whether we assume that the atoms remain excited for a definite constant time or that the number still excited at  $x$  of  $N$  at  $x=0$  is of the form  $KNe^{-cx}$ .

These remain excited until  $\eta$ , where  $\eta - \xi = \lambda$ , at which in an element equal to  $\delta\xi$  they all begin to emit.

$\therefore$  Number beginning to emit in  $\delta\xi$  at  $\eta$  [ $\eta - \xi = \lambda$ ]

$$\begin{aligned} &= \frac{N}{L} \left(1 - \frac{\xi}{d}\right) e^{-\frac{\xi}{L}} \delta\xi, \\ &= \frac{N}{L} \left(1 - \frac{\eta - \lambda}{d}\right) e^{-\frac{\eta - \lambda}{L}} \delta\eta. \end{aligned}$$

Intensity of light emitted at  $d$  due to these

$$= \frac{KN}{L} \left(1 - \frac{\eta - \lambda}{d}\right) e^{-\frac{(\eta - \lambda)}{L}} e^{-\frac{d - \eta}{l}}.$$

$\therefore$  Total intensity of light-emission at  $d$  due to atoms charged at A

$$\begin{aligned} &= K \int_{\lambda}^d \frac{N}{L} \left(1 - \frac{\eta - \lambda}{d}\right) e^{-\frac{(\eta - \lambda)}{L}} e^{-\frac{(d - \eta)}{l}} d\eta, \\ &= K \left\{ \frac{Nl^2L}{d(L-l)^2} e^{\frac{\lambda - d}{L}} - \frac{Nl}{L-l} e^{\frac{\lambda - d}{L}} \right. \\ &\quad \left. + \frac{N\lambda l}{d(L-l)} e^{\frac{\lambda - d}{L}} - \frac{Nl^2L}{d(L-l)^2} e^{\frac{\lambda - d}{L}} \right\}. \end{aligned}$$

The intensity of light at  $d$  due to atoms emitting at entrance to field

$$= KN_1 e^{-\frac{d}{l}}.$$

Number of atoms per c.c. excited at entrance to field is  $N_2$ . Number of those beginning to emit in element  $\delta\xi$  at  $\xi$  if  $\xi < \lambda$ ,

$$= \frac{N_2}{\lambda} \delta\xi.$$

Intensity of light at  $d$  due to these

$$= \frac{KN_2}{\lambda} e^{-\frac{(d - \xi)}{L}} \delta\xi.$$

$\therefore$  Total intensity of light-emission at  $d$  due to atoms excited at entrance to field

$$\begin{aligned} &= K \int_0^{\lambda} \frac{N_2}{\lambda} e^{-\frac{(d - \xi)}{L}} d\xi. \\ &= \frac{KN_2 l}{\lambda} e^{-\frac{d}{L}} \left( e^{\frac{\lambda}{L}} - 1 \right). \end{aligned}$$

∴ Total intensity of emission at  $d$  due to all sources when magnetic field used

$$= K \left[ \frac{N^2 L}{d(L-l)^2} e^{\frac{\lambda-d}{L}} - \frac{Nl}{L-l} e^{\frac{\lambda-d}{l}} + \frac{N\lambda l}{d(L-l)} e^{\frac{\lambda-d}{L}} \right. \\ \left. - \frac{Nl^2 L}{d(L-l)^2} e^{\frac{\lambda-d}{l}} + N_1 e^{-\frac{d}{l}} + \frac{N_2 l}{\lambda} e^{-\frac{d}{l}} \left( e^{\frac{\lambda}{l}} - 1 \right) \right] \quad (i.)$$

As observations were made at about 7 cm. behind the cathode, equilibrium must have been almost reached between the various constituents of the beam.

$$\therefore \frac{N}{L} = \frac{N_1}{l} = \frac{N^2}{\lambda} = \text{some constant "a."}$$

$$\therefore N = aL : N_1 = al \quad \text{and} \quad N_2 = a\lambda.$$

Substituting these values for  $N$ ,  $N_1$ , and  $N_2$  in (i.), we obtain

$$(i.) = K \left[ \frac{aL^2 l^2}{d(L-l)^2} e^{\frac{\lambda-d}{L}} - \frac{aLl}{L-l} e^{\frac{\lambda-d}{l}} + \frac{aL\lambda l}{d(L-l)} e^{\frac{\lambda-d}{L}} \right. \\ \left. - \frac{aL^2 l^2}{d(L-l)^2} e^{\frac{\lambda-d}{l}} + al e^{\frac{\lambda-d}{l}} \right] = I'_B.$$

The intensity at  $A$  when no magnetic field used is proportional to  $N_1$ , the concentration of emitting particles at  $A$ .

$$\therefore \text{Intensity at } A = KN_1 = Kal = I_A.$$

Let  $T$  be the time of excitation and  $t$  the time of emission.

$$\text{Then} \quad \lambda = TV \quad \text{and} \quad l = tV.$$

Substituting these values for  $\lambda$  and  $l$  in (i.), we get

$$I'_B = KatV \left[ \frac{L e^{\frac{TV-d}{L}}}{d(L-tV)^2} (LTV - TtV^2 + LtV) \right. \\ \left. + \frac{e^{\frac{TV-d}{tV}}}{d(L-tV)^2} (dt^2V^2 - L^2tV - tVLd) \right].$$

Also

$$I_A = Kal = KatV.$$

$$\therefore \frac{I'_B}{I_A} = \frac{L e^{\frac{TV-d}{L}}}{d(L-tV)^2} (LTV - TtV^2 + LtV) \\ + \frac{e^{\frac{TV-d}{tV}}}{d(L-tV)^2} (dt^2V^2 - L^2tV - tVLd). \quad (ii.)$$

In the steady state without the magnetic field the intensity of the moved line at A will be almost equal to that at B. Thus we may put  $I_A = I_B$ .

$$\therefore I_B'/I_B = I_B'/I_A = \text{eq. (ii.)}$$

Eq. (ii.) therefore represents the ratio of the intensity at B with and without the use of the magnetic field. If by some means we could measure experimentally the ratio  $I_B'/I_B$  for various velocities of the positive rays, knowing  $L$  from Ruchardt's work, we could determine the values for  $T$  and  $t$  which on substitution in eq. (ii.) make it agree best with the measured values of  $I_B'/I_B$  in the different cases. It was for this reason that the Ilford wedge-screen was used as it measures directly the ratio  $I_B'/I_B$ . Let  $x$  be the shift of the wedge required to retain equality of intensity of the two halves of the slit in the spectroscope on switching on the magnetic field.

Then

$$\log_{10} I_B'/I_B = -\mu x,$$

where  $\mu$  is the index of the wedge.

There are two implicit assumptions made in the mathematical analysis above:—

(i.) That  $I_A$  does not change on excitation of the magnet.

(ii.) That the effect of the rays which lose an electron between A and B on the intensity of the moved line at B is small.

We shall consider these two points in detail.

(i.) The intensity at A does not necessarily remain the same when the magnet is excited. Suppose the intensity at A becomes  $cI_A$  where  $c$  is a fraction. The intensity at B will become  $cI_B'$ . Now the wedge measures the ratio of the intensities at A and B with the magnetic field divided by the ratio of the intensities without the field. That is, the wedge-shift gives us the value of

$$\frac{cI_B'/cI_A}{I_B/I_A} = \frac{I_B'}{I_B}.$$

The use of wedge therefore nullifies any error due to the change in the intensity at A on switching on the magnetic field.

(ii.) In the mathematics we assume that few of the moving ions produced between A and B emit at B. The graph obtained in the case of the higher velocities points to a time of excitation of about  $10^{-8}$  sec. Ions produced within the region AB have to regain an electron and pass through the excited condition before they can emit. With the

slowest rays ( $7$  or  $8 \times 10^7$  c/s) used this is sufficient to take them beyond B in the excited condition, provided they were not formed in the immediate neighbourhood of A. Those formed near A would have a very small effect, but the magnetic field was strong enough to deflect all ions formed near A into the earthed tube S between A and B.

Table II. gives a set of measurements with the value of  $I_B'/I_B$  in the column on the right calculated from the observed shift of the wedge.

TABLE II.

Velocity.	Wedge-shift.	$I_B'/I_B$ .
$1.3 \times 10^8$ c/s	.66 cm.	.64
$1.2 \times 10^8$ c/s	.53 "	.70
$1.02 \times 10^8$ c/s	.54 "	.69
$0.95 \times 10^8$	.67 "	.64
$0.92 \times 10^8$	.72 "	.62
$0.83 \times 10^8$	.63 "	.66
$0.80 \times 10^8$	.53 "	.70
$0.79 \times 10^8$	.52 ,	.71

The magnitudes of the times of emission and excitation which make eq. (ii.) agree best with the measured values of  $I_B'/I_B$  for the various velocities are found to be  $2 \times 10^{-8}$  sec. and  $0.75 \times 10^{-8}$  sec. respectively. In Table III. are given the velocity, the observed value of  $I_B'/I_B$  and that calculated from eq. (ii.) on the assumption that  $t$  is  $2 \times 10^{-8}$  sec. and  $T$   $0.75 \times 10^{-8}$  sec. It will be seen that the measured and calculated values of  $I_B'/I_B$  agree remarkably well, considering the rate at which eq. (ii.) varies with the values for the times of emission and excitation used in calculating it.

TABLE III.

Velocity.	$I_B'/I_B$ (meas.).	$I_B'/I_B$ (calcul.).
$1.3 \times 10^8$	.64	.68
$1.2 \times 10^8$	.70	.74
$1.02 \times 10^8$	.69	.72
$0.95 \times 10^8$	.64	.67
$0.92 \times 10^8$	.62	.69
$0.83 \times 10^8$	.66	.63
$0.80 \times 10^8$	.70	.60
$0.79 \times 10^8$	.71	.60

We thus find by the second method that the time of emission is about  $2 \times 10^{-8}$  sec., and the time of excitation  $0.75 \times 10^{-8}$  sec. The latter agrees as well as could be

expected with that found by the first method, viz.  $10^{-8}$  sec. The difference is small, and can easily be accounted for, as the no wedge-shift method tends to make the result for the time of excitation slightly too big. This is due to the fact that, as the velocity of the positive rays increases, the intensity of the moved line of  $H_B$  rapidly diminishes, making observations difficult and, at the same time, the wedge-shift becomes smaller. The result of these two effects is that, before the wedge-shift should be zero, the intensity of  $H_B$  and the wedge-shift have both become so small that the latter is almost undetectable. Thus we declare that no shift of the wedge is required for less than the real minimum velocity necessary for no change in intensity to occur at B on switching on the magnetic field. The time of excitation is found by dividing the distance between A and B by the critical velocity which, being probably slightly too small, makes the time of excitation correspondingly too large.

No published paper has described a method for determining the time of excitation of any line of the Balmer Series of Hydrogen without the intervention of the time of emission. The entrance of these two times into any expression for the intensity of light-emission from a beam of positive rays makes discrimination between them difficult, if not impossible. By the no wedge-shift method, however, we can determine definitely the time during which an electron remains in an excited orbit without any regard being paid to the time it takes to liberate its quantum of radiation. Having found the time of excitation in this way, the time of emission may be determined explicitly by the second method. No ambiguity between the times of emission and excitation will then arise, as the latter must correspond with the value found for the time of excitation by the no wedge-shift method. Dempster obtains  $5 \times 10^{-8}$  sec. as the sum of the times of emission and excitation. The present paper gives a value of about  $3 \times 10^{-8}$  sec. There is, therefore, consistency between the two measurements; but whereas up to the present the time of excitation has been assumed to be extremely small and almost a different way of looking at the time of emission, the above results indicate that it is distinct from the time of emission and comparable with it in magnitude. Stark \* fired fast-moving positive rays into a space where the Electric Potential Gradient was very large. He found that the Stark effect at any point corresponded with the field very close to that point. This would indicate, in my opinion, a very short time of emission

\* *Ann. d. Phys.* xliii. p. 968 (1914); xlviii. p. 194 (1915).

and a rather longer time of excitation. We must assume a time of excitation in this case to bring Stark's measurements into agreement with the rate of decay of emission in the beam as found by Wien. If there were no time of excitation, the rate of decay would be much larger than that observed. Another factor which points to a finite time during which an electron remains in an excited orbit is the definite frequency of the emitted spectrum line. This entails a sharply-determined quantized motion of the electron in the excited orbit which, I think, requires a finite time for the electron to assume it.

I should like to express my sincere thanks to Prof. G. P. Thomson, whose many suggestions and kindly criticisms have made possible the publication of this paper. Thanks are also due to the Robbie Trustees, Aberdeen University, for a grant during the progress of the work, and to Mr. S. A. McKay for valuable help in the taking of measurements.

National Physical Laboratory,  
Teddington,  
Jan. 24, 1926.

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### XCIX. *Ignition of Gases by Sudden Compression.*

*By* H. T. TIZARD, F.R.S., and D. R. PYE\*.

[Plate XVII.]

1. **I**T is well known that the ignition of gases by sudden compression can be qualitatively explained by the theory that at the temperature of compression the gases react at such a rate that heat is evolved by the reaction faster than it is lost by conduction to the walls of the vessel. In a previous paper † this theory was developed on a quantitative basis, and it was shown that with simple assumptions it could be shown to account completely for the delay that takes place between the attainment of the maximum compression temperature and the actual initiation of the explosion. From observations of the delay period at different temperatures above the minimum ignition temperature, it was found possible to deduce approximately the temperature coefficient of the reaction, and from this to calculate the change in ignition temperature when the rate of loss of

\* Communicated by the Authors.

† Phil. Mag. July 1922.

heat was altered arbitrarily by stirring the gases violently during compression. The object of the experiments described in this paper was to examine the theory more closely and to clear up some doubtful points.

2. For this purpose a modified apparatus was designed and built, which has the advantage that it can be used for experiments with simple gases, such as hydrogen, which have fairly high ignition temperatures in the presence of air or oxygen. If the initial temperature of the gas before compression is low, high compression temperatures can only be reached by employing high degrees of compression. Thus Dixon and Crofts showed that a mixture of hydrogen and air initially at room temperature had to be compressed in the ratio of 15:1 before ignition occurred. The excessive compression pressures so produced cause considerable experimental difficulties when the compression cylinder is large. To avoid these difficulties, the initial temperature of the gas must be high. In our old apparatus it was impossible to heat the gases initially to a temperature much above  $60^{\circ}$ , since higher temperatures destroy the cup-leathers on the piston, which contain the oil seal necessary to keep the cylinder gastight. In our new apparatus this was overcome by arranging two cylinders in tandem. The upper cylinder contains a plain closely-fitting plunger, and it can be heated to  $150\text{--}180^{\circ}\text{C.}$  by an oil jacket. The lower cylinder is always kept at room temperature, and its piston is fitted with the double cup-leather and oil seal described in the earlier paper. On compression, the pressures in the lower and upper cylinders balance, so that there is no tendency for the gas in the upper working cylinder to escape. The general arrangement is shown in the diagram fig. 1. The indicator of the Collins type, used to record the changes of pressure of the gas, was described in detail by Pye\*. The reproductions of records given in this paper are enlarged about eight times.

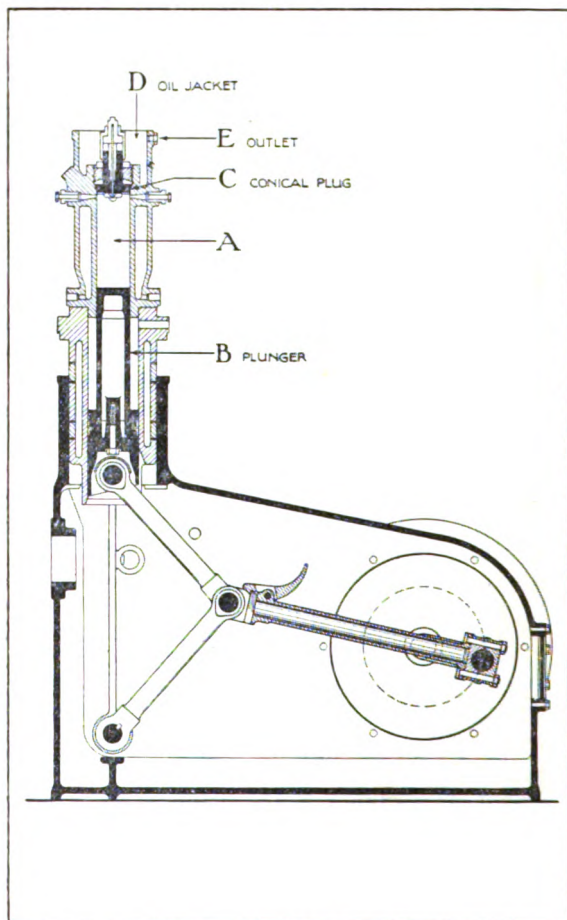
3. The working cylinder has a diameter of 3 inches, and the stroke of the piston is 8 inches. The machine can be arranged to compress in a ratio of either 6:1 or 9:1. But for the cylinder construction the apparatus is practically the same as the previous apparatus. Special attention may be drawn to the method of compression, which ensures that the piston cannot move outward and expand the gases after the maximum compression has been reached. This is an important feature of the apparatus, for, as the delay before ignition occurs is often as long as half a second, the volume

\* 'Journal of Scientific Instruments,' March 1925.



of the compressed gases must be kept constant during this time. It is difficult, however, with an apparatus of this type to compress the gases very suddenly, owing to the

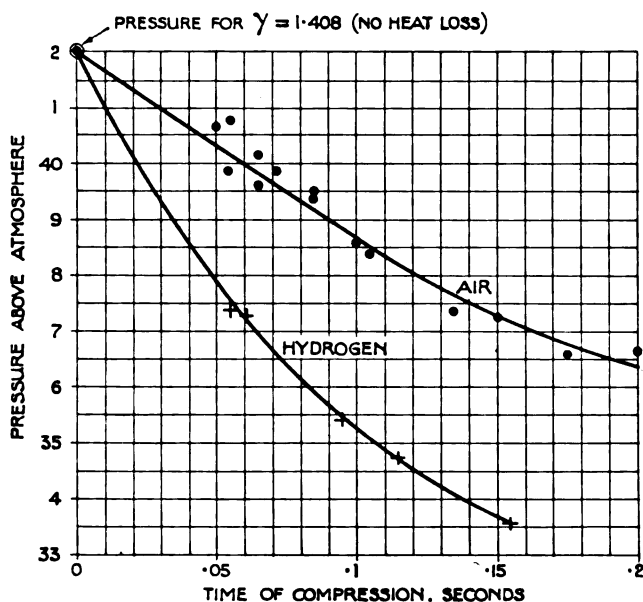
Fig. 1



inertia of the moving parts. We found that it was necessary for the time of compression to be greater than 0.05 second to avoid fracture of the moving parts; indeed, fracture occurred on one occasion when the time was as short as this, so that as a rule the time of compression was kept constant at 0.14 second.

4. Under these conditions the maximum pressure reached by compression is always considerably lower than that calculated on the assumption that compression is adiabatic. For instance, the pressures when air and hydrogen are compressed in the ratio of 6.09:1 was found to be 11.7 atmospheres for air and 10.7 atmospheres for hydrogen, when the time of compression was 0.1 second. The corresponding adiabatic compression pressure is calculated to be 12.5 atmospheres ( $\gamma=1.4$ ). The difference may be due to (a) gas leakage, (b) an increase in the average specific heat

Fig. 2.



of the gases due to the presence of water vapour or oil vapour, (c) loss of heat during compression. Special experiments showed that the possible effects of (a) and (b) were negligible. The rate of gas leakage was shown by these experiments to be less than 1 per cent. of the rate of fall of pressure due to cooling, while the compression of damp air when the surfaces of the piston and cylinders were freely lubricated with castor oil gave a value for the compression pressure only slightly less than that observed when dry air was compressed in a clean cylinder. That the pressure difference would be entirely accounted for,

within the limits of experimental error, by the loss of heat during compression was shown by carrying out a series of compressions of air and hydrogen at different rates of compression. The results of these experiments are shown in fig. 2, the pressures reached being expressed in arbitrary units—1 atmosphere being equal to 3.64 units. The lines through the observed points, when produced backwards, cut the pressure axis (which corresponds to instantaneous compression and no heat loss) at just about the “adiabatic” pressure.

It is of some interest to note here that in an internal combustion engine operating at 1200 r.p.m. the time of compression is  $1/40$ th of a second. From the results shown in fig. 2, it appears that the loss of heat during the compression would not be greater than that corresponding to a 2 per cent. loss in compression temperature, even with a jacket temperature the same as that of the charge at the beginning of compression. For all practical purposes, therefore, it is safe to assume adiabatic compression in a high-speed internal combustion engine.

5. It is thus clear that the average temperature of a gas after compression will always be considerably lower than the adiabatic compression temperature. This raises the question whether the average temperature or the calculated adiabatic temperature should be taken as the ignition temperature when ignition occurs. In the work carried out by Dixon and others no pressure records were taken, and the calculated adiabatic temperature has therefore always been chosen. In our previous paper we gave our results in terms of the average temperature reached on compression, but we pointed out the uncertainty involved. This question has now been examined more closely.

The assumption that the gas after compression is uniformly at the same temperature except within a region quite close to the containing walls is clearly unjustifiable, though it may be sufficiently near the truth for all practical purposes. The more highly turbulent the gas, the more uniform will be the temperature. If it were uniform, we should expect the slow chemical reaction during the pre-ignition period to take place throughout the gas. If this were so, the pressure reached on compression would either remain constant or rise slightly during the delay period; and when ignition occurred the whole mass of gas would ignite at once. Dixon's photographs of ignition after compression throw light on this point. He showed that the start, as well as the spread, of ignition was very

indefinite, when compared with ignition started by a spark. On the other hand, it is quite clear from his photographs that the whole mass of gas does not ignite at the same moment. Our pressure records show that, though in some cases the compression pressure remains constant or rises slightly during the delay period, these cases only occur when the compression temperature is substantially higher than that corresponding to the least compression necessary to cause ignition. In fig. 3 (Pl. XVII.) a record is reproduced showing practically constant pressure during the delay period. In this case the time of compression was slow. In the majority of cases at or near the minimum ignition temperature there is a fall of pressure during the delay period, such as is shown on the record fig. 4 (Pl. XVII.) between 0.14 (end of compression) and 0.39 seconds, and this fall can occur at a rate which is practically the same as the rate of fall of pressure when no ignition occurs.

For instance, of twelve experiments on mixtures of octane and air under different conditions of temperature and mixture strength, eight ignited and four did not. The observed falls in pressure during the first and second, 1/10th of a second after the completion of compression are shown in the following table:—

TABLE I.  
Pressure drop from  $P_{\max}$  in lb. per sq. in.

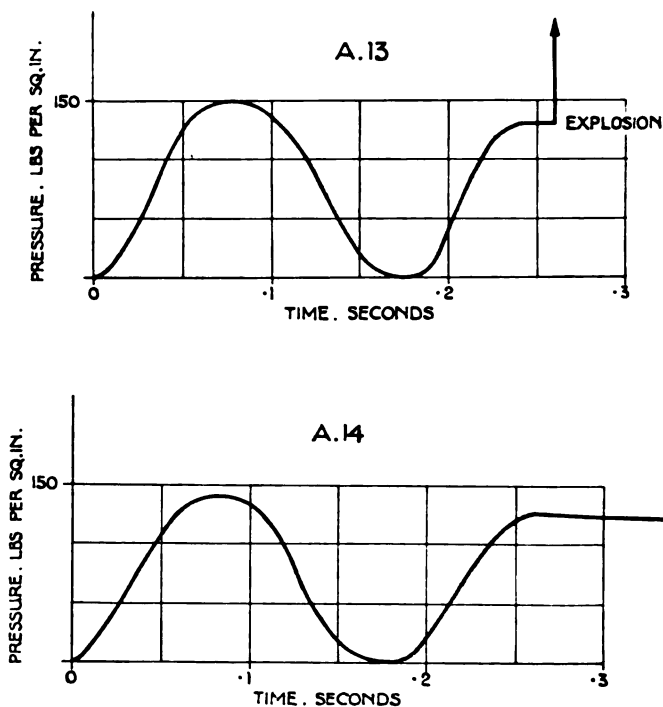
Non-igniting records.			Records on which explosion subsequently occurred.		
1st 1/10".	2nd 1/10".	1st 1/5".	1st 1/10".	2nd 1/10".	1st 1/5".
8.5	6.9	15.4	5.3	5.6	10.9
8.9	7.7	16.6	10.9	7.3	18.2
9.7	6.5	16.2	11.3	7.3	18.6
9.3	5.7	15.0	9.7	6.1	15.8
			8.9	6.5	15.4
			11.3	6.5	17.8
			13.3	4.9	18.2
			8.9	7.7	16.6
	Mean .....	15.8		Mean .....	16.6

It will be observed that the average rate of fall of pressure during 1/5th of a second after compression is the same, within the limits of experimental error, whether the

mixture subsequently ignited or not. The actual amount of heat generated by combustion during the delay periods must, therefore, have been negligibly small.

Two other experiments with mixtures of ether and air are of especial interest in this connexion. In these experiments the clip of the machine which should hold the piston fixed at the end of compression failed to work. Instead of being subjected to a single compression, the mixture was alternately compressed and expanded, and only on the second compression was the piston locked in place. The records appear as fig. 5. In A.13 ignition occurred,

Fig. 5.



in A.14 it did not. The initial temperatures were the same in each case, but there was a greater proportion of ether in the mixture used in A.14. The specific heat was therefore higher, and the average temperature reached on the first compression lower. But the average temperature reached after the second compression of A.13 is lower than that after the first compression of A.14, owing

to the loss of heat caused by the two compressions. The fact that the mixture nevertheless ignited is most easily explained on the assumption that, in spite of the low average temperature, a small portion of the mixture reached a considerably higher temperature on the second compression.

6. These observations on the rate of fall of pressure during the delay period are in agreement with Dixon's photographs, and lead to the conclusion that ignition does not occur simultaneously throughout the gas. Our own experiments go further, in that they show that ignition can occur even when the main body of the gas has cooled down to a temperature very far below the average temperature immediately after compression. Hence it is clear that as a rule ignition is initiated by quite a small portion of the gas; and the question at once arises whether the quantitative results on the delay to be expected under different conditions, and on the temperature coefficients of the gas reactions derived by the method indicated in our previous paper, can be justified. The main point at issue is the rate at which the portion of the gas which is going to ignite first is losing heat, and the theory as developed assumes that it is losing heat at the same rate as the average rate for the whole gas. This cannot be strictly true, and therefore the conclusions which rest on such an assumption equally cannot be strictly true. But, nevertheless, the rate at which the nucleus of combustion is losing heat must bear some relation with the average rate—that is to say, it must increase when the average rate increases,—and therefore we should have no hesitation in accepting the quantitative results as relatively true. This is borne out by further experiments, which show how closely the observed ignition temperatures of the substances dealt with agree with the observed temperatures in the old and larger apparatus when the difference in the rate of loss of heat, which is considerable, is taken into account.

7. For this purpose it was first necessary to compare the rates of loss of heat after compression in the new and old apparatus. It was shown in the previous paper that the rate of loss of heat was practically proportional to the difference between the average temperature of the gas and the temperature of the water, and could therefore be expressed by the equation

$$-\frac{d\theta}{dt} = \alpha(\theta - T),$$

$\theta$  being the gas temperature and  $T$  the wall temperature.

It was shown that the factor  $\alpha$  was not quite constant, as the gas temperature fell, but nearly so, particularly when the specific heat of the gas was high\*. The effect of running the fan in the combustion space was to increase the cooling factor  $\alpha$  about two to three times.

In the present series of experiments both time and pressures could be measured with greater accuracy than previously, and the records gave regularly varying values of  $\alpha$  as shown in the following Table II., where results are given for cooling curves after compression in the ratio of 6:1 of air and hydrogen, with and without the stirring fan in action.

TABLE II.  
Cooling Factor,  $\alpha$ .

Time interval from moment of maximum pressure.	Air.		Hydrogen.	
	Without fan.	With fan.	Without fan.	With fan.
·05	1·43	2·72	3·13	6·0
·1	1·27	2·44	3·06	5·4
·15	1·20	2·30	2·80	4·9
·2	1·10	2·21	2·67	4·55
·3	1·02	2·11	2·43	4·00
·4	·95	2·00	2·20	3·57
·5	·89	1·90	2·04	3·27
·75	·805	1·70	1·7	2·74
1·0	·765	1·62	1·65	2·40

These figures show in the first place that the rate of heat loss is by no means proportional to  $(\theta - T)$ , and a comparison of the results with and without the fan seems to show that the falling off with time of values of  $\alpha$  is not due to the dying down of turbulence in the cylinder, since both with and without the fan the value of  $\alpha$  falls in roughly the same ratio during the first second.

A comparison with values of the cooling factor given in the previous paper† and obtained on the earlier machine shows that the new machine gives in all cases considerably higher values. The earlier figure for the cooling factor of air without the fan at 6:1 compression was about 0·76. Rather higher values would be expected with the new machine, owing to the combustion space having a greater ratio of surface to volume.

\* Compare Tables I. and IV, Phil. Mag. July 1922, pp. 92 & 101.

† *Loc. cit.*

8. Table III. gives the results of typical experiments by which the behaviour of mixtures of ether and air on compression in the old and new apparatus can be compared. The results with the old apparatus are quoted from the previous paper.

TABLE III.

	Compression ratio.	Initial temperature.	Delay before ignition.	Cooling factor.
Old apparatus without fan.	4.83 5.02	24° C. 23° C.	No ignition. 0.41 sec.	0.47 —
Old apparatus with fan.	5.73 5.94	24° C. 22° C.	No ignition. 0.13 sec.	1.28 —
New apparatus without fan.	6.09 6.09	24° C. 24° C.	No ignition. 0.11 sec.	1.3 —

In the first of the two quoted experiments with the new apparatus, the amount of ether present in the mixture was greater than in the second. Owing to the higher specific heat of the mixture, the compression temperature is lower. This accounts for the fact that no ignition took place, although it occurred in the second experiment quoted. In this experiment the strength of the mixture was practically the same as in the experiments with the old apparatus. The cooling factor was calculated from the rate of fall of pressure after compression in the first experiment. The figure given is the average over the first 0.3 second after compression. It is practically the same as the cooling factor calculated for the old apparatus when the fan was running. It will be noticed that the compression ratios necessary to cause ignition under these conditions are practically the same, and were very considerably higher than the compression ratio necessary to cause ignition in the old apparatus when the fan was not running and the rate of cooling after compression was only about one-third as great.

9. Similar results obtained with mixtures of heptane and air are shown in Table IV.

TABLE IV.

	Compression ratio.	Initial temperature.	Observed compression pressure.	Calculated average compression temperature.	Delay before ignition.	Cooling factor.
Old apparatus without fan.	5.55 6.56	51° C. 35° C.	141 176	280° C. 282° C.	No ignition. 0.58 sec.	0.49 —
Old apparatus with fan.	6.13 6.33	59°-55° C. 59°-5° C.	161 165	310° C. 313° C.	No ignition. 0.13 sec.	1.47 —
New apparatus without fan.	6.09 6.09	64° C. 66° C.	153 153	295° C. 298° C.	No ignition. 0.45 sec.	1.23 —



It will be observed that the ignition temperatures and the cooling factors correspond. A more accurate comparison can be made by calculating from the observed ignition temperature in the old apparatus (without fan) what the ignition temperature in the new apparatus should be when the difference in the rate of cooling is taken into account. According to the equation developed in the previous paper, the ignition temperatures should be connected by the equation

$$\log \frac{Q_0'}{Q_0} = \frac{b}{T_0} \left( 1 - \frac{T_0}{T_0'} \right),$$

$T_0$  and  $T_0'$  being the ignition temperatures when the rate of loss of heat is  $Q_0$  and  $Q_0'$ .

$$\frac{Q_0'}{Q_0} = \frac{\alpha'(T_0' - \theta')}{\alpha(T_0 - \theta)},$$

$\alpha, \alpha'$  being the cooling factors, and  $\theta, \theta'$  the wall temperatures.

Hence, from the figures given above,  $\frac{Q_0'}{Q_0} = 2.6$  approx.

The factor " $b$ " corresponds to the temperature coefficient of the reaction, and was obtained by measuring the length of the delays before ignition at different temperatures. It was shown that  $b/T_0 = 10$ .

Hence

$$\frac{T_0}{T_0'} = 1 - \frac{1}{10} \log \frac{Q_0'}{Q_0}$$

$$= .96,$$

$$T_0' = \frac{553}{.96} = 577 = 304^\circ \text{C.}$$

The actual observed temperature of ignition was  $298^\circ \text{C}$ . The agreement is therefore good.

10. These experiments, and many other experiments we have made with substances of the same type which are liquid at the ordinary temperatures, lead to the general conclusion that the ignition of such substances can be quantitatively explained on the simple thermal theory that the reaction between the compounds and oxygen proceeds at a rate which is conditioned by temperature, and that ignition or non-ignition depends on the rate of loss of heat at this temperature. If the rate of loss of heat is measured, the ignition temperature under one set of conditions can be calculated from the observed ignition temperature under other conditions. The consistency of behaviour of such

substances is marked ; ignition always occurs if the limiting temperature is reached on compression. When mixtures of ignitable *gases* and air are similarly compressed we do not find such consistency ; and temperature and rate of loss of heat do not seem sufficient to account for the phenomena observed. The results of experiments on hydrogen and acetylene will be given in another paper.

11. For the sake of completeness, Table V. contains the chief results of a large number of experiments with pure pentane, hexane, heptane, and octane. With the exception of heptane, the pure specimens were kindly lent to us by Professor Sydney Young. In all these experiments the compression ratio was 6.09 : 1, the compression temperature being controlled by varying the initial temperature.

TABLE V.

Substance.	Initial temperature.	Minimum "average" temperature of compression to produce ignition.
Pentane.....	91.5 (90.5)	316° C.
Hexane .....	78 (77)	307° C.
Heptane.....	66 (64)	298° C.
Octane .....	60.5 (59)	297° C.

The figures in brackets show the initial temperatures in experiments when ignition did not occur on compression. The "average" self-ignition temperatures are calculated from the observed compression pressures. Owing to absence of any accurate data on the mean specific heats of the vapours over the range from the initial temperature to the compression temperature, it is impossible to calculate accurately the corresponding "adiabatic" ignition temperatures ; but from the approximate calculation made in paragraph 19 of the previous paper it may be concluded that the temperatures of adiabatic compression are not more than 50° C. above the average temperatures given above.

The rates of cooling after compression are practically the same for all these substances. The cooling factor is approximately 1.3. It will be noticed that these experiments show that the ignition temperatures of the paraffin hydrocarbons decrease as the molecular weights increase. This is in agreement with the observation that paraffin hydrocarbons tend to "detonate" more easily in internal combustion engines, the higher their boiling-points.

C. *Time and Chance.* By NORMAN CAMPBELL, Sc.D.\*

## SUMMARY.

VERY general considerations indicate that a revision of classical conceptions of time is necessary. The view is suggested that time is a statistical conception; that while individual neighbouring events have a definite time-order, any temporal magnitude, such as velocity, interval, or frequency, is significant only with regard to statistical aggregates, and represents a probability of transition characteristic of the individual elements.

The bearing of this suggestion upon outstanding problems is considered:—(a) The lack of “reciprocity” in the interaction of an atom and charged particle (Bohr); (b) the interaction between matter and radiation, and the conflict between quantum and wave theory; (c) quantum mechanics, with special reference to the work of Heisenberg. In no case is any definite theory offered; but it is argued that a theory on these lines must be physically possible, while the mathematical possibility can be discussed only by those more skilled in analysis.

*Introduction.*

IN a letter to ‘Nature’ a few years ago† it was suggested that the difficulties of reconciling classical and quantum theories might arise from the introduction into the latter of temporal conceptions derived from the former, and that apparent inconsistencies entered because “time” has no meaning within the atom. No attempt to develop this suggestion has been made either by myself or by others, though Bohr‡ in his recent papers has hinted (of course quite independently) that any formulation of quantum principles in terms of time and space may be impossible. But I venture to raise the matter again, not because I have any definite timeless theory to propose, but because it seems to me that one feature of Heisenberg’s§ most attractive attempt to formulate a quantum mechanics has been accepted without as much consideration as it deserves.

Heisenberg starts with the determination to include for his formulation only those quantities that are “*principiell beobachtbar*” ||. Among the quantities which he takes as

\* Communicated by the Author.

† N. R. Campbell, ‘Nature,’ cvii. p. 170 (1921).

‡ N. Bohr, *Zeit. f. Phys.* xxxiv. p. 142 (1925).

§ W. Heisenberg, *Zeit. f. Phys.* xxxiii. p. 879 (1925).

|| Born & Jordan (*Zeit. f. Phys.* xxxiv. p. 858, 1925) replace “*principiell beobachtbar*” by “*wirklich augemessen*.” Of course the objections apply quite as strongly to the second phrase.

satisfying his criterion is  $\nu(mn)$ , the frequency of radiation emitted associated with the transition from a stationary state  $m$  to a stationary state  $n$ .

It is dangerous to deny any proposition involving such an exceedingly ambiguous adverb; but it is by no means obvious that if a distinction is to be made between quantities that are observed and those that are not, the frequency of radiation falls into the former class. For determinations of that quantity involve experiments of two totally different kinds: first, interference experiments in which no temporal magnitude is measured nor any change with time observed; second, experiments on the velocity of light in which temporal magnitudes are observed, associated, not with any atomic systems or any changes to which quantum principles would be expected to apply, but with gross material bodies, such as planets or revolving mirrors. Now, as the whole question at issue is why principles which apply to these gross material bodies do not apply to individual atoms or the radiation which they emit, it is surely stretching the meaning of a very accommodating word beyond its elastic limit to say that we have observed "in principle" the frequency belonging to the latter when we have only actually measured a frequency belonging to the former.

Heisenberg, in fact, assumes that all our classical conceptions of time can be transferred without alteration to atomic systems. This is precisely the proposition which seems to me highly dubitable. We shall consider later whether it is really essential to his theory; first it will be convenient to consider an alternative. The view I want to suggest here is that time, like temperature, is a purely statistical conception, having no meaning except as applied to statistical aggregates; that a temporal magnitude, such as an interval or a frequency, is a statistical magnitude and that there is no such thing as the frequency of an atomic change or the interval between atomic events; that time and chance are merely two aspects of the same thing; and that the ultimate magnitude, the statistical average of which is a temporal magnitude, is the probability of a change or (with a slightly more definite connotation) of a transition.

### *Outline of the Theory.*

At the risk of being dubbed metaphysical, perhaps I may start from (but discuss very briefly) the considerations which first forced the idea on my attention, although they are much deeper and are much more general than the particular

problems of quantum theory. They arise when we inquire on what evidence we assert our knowledge of any "routine"; that is to say, a collection of invariably associated events invariably ordered in time, such as that described by the law that a body falls with uniform acceleration. In order that a routine may be established, several examples of it must be observed; repetition involves separation in time; the examples must themselves have a time-order. The routines actually observed must have beginnings and ends: and though the internal time-relations of all events in the routine may be the same, the routines are distinguished by the relations of their terminations. What justification have we, then, for asserting that the various examples of the routines are the same, that there is repetition, and that this repetition establishes the routine?

The answer is, I think, that what we profess to establish in such cases is a numerical law of a certain form, which is obeyed by all examples of the routine. This law is valid over an infinite range so long as the conditions which determine it are unaltered. Routines are infinitely extended and have no terminations; the terminations actually observed are not parts of the routine, but represent the intrusion of something that is not a routine. This disturbing element, if it is not of a nature necessarily inaccessible to science, is chance: if we are to give any account at all of the actual terminations observed, we must say that they are due to chance.

That is a very summary account of a very difficult problem. The point I want to make is that time and chance are inevitably associated, because we cannot give any adequate account of routines (on which depend all temporal magnitudes) without recognizing also the influence of chance. We must regard changes in time as of two kinds, the regular kind which can be grouped into routines, and the irregular kind which are due to pure chance; there is no evidence for the former unless at the same time we admit the existence of the latter. The suggestion that we are considering, that time is merely statistical, is simply a proposal for abandoning the first kind of change and for effecting a great simplification in our ideas by recognizing only one kind of time change, namely that due to chance.

The proposal receives strong support from the most fundamental proposition of Einstein's formulation of quantum principles. Chance enters in determining transitions between stationary states. But stationary states are stationary; they represent the absence of all change and therefore the absence of everything to which the concept of time can be

applicable. Chance does not initiate routines, as in the dualistic view which has been generally accepted; it initiates only the absence of change. Changes in time are all changes by chance; there is no such thing as a routine in systems to which quantum principles are applicable.

In the study of radioactivity (to which, as Rosseland has insisted\*, quantum principles must be applicable) we have actual experimental knowledge of such a state of affairs. There is no routine whatsoever describing the disintegration of a single atom; it undergoes changes by pure chance, and in the interval between changes by chance nothing whatsoever happens. In fact, the very use of the word "interval" introduces ideas that are really foreign to the facts. If we were really observing a single atom only and had no experience other than that derived from this atom, we could only say that the successive changes occurred in a certain time-order, and that one of these changes occurred in the interval between its predecessor and successor. There could be no question of an interval between successive changes; that would only arise if we observed a second atom and noticed its changes occurring between those of the first atom. But though by such comparison of two atoms we might arrive at the conception of an interval between changes, we could not possibly arrive at a measure of that interval; for in successive repetitions of the comparison the changes in one atom would not occur in the same places in the time-order of the other, still less would the more complex conditions be fulfilled that are demanded for the measurement of periods†.

Measurement of intervals is possible only when large collections of atoms are observed; actually we could use considerable masses of radioactive substances as clocks. The exact details of the process need not be described, but it is important to make sure that the proposition on which it ultimately depends can be stated in statistical terms without the introduction of temporal concepts (other than that of temporal order) applicable to the individual atoms. The proposition is this. Let there be a very large number  $N$  of atoms  $A$  and a very large number  $M$  of atoms  $B$ . Let  $n$  changes in  $A$  be observed and  $m$  in  $B$ , these changes being such that all the  $n$  changes (and no other changes of this type) occur between the first and last of the  $m$  changes, or vice versa. Then it is an experimental fact that, if  $n$  and  $m$  are increased indefinitely, while the ratios  $n/N$  and  $m/M$  are

\* S. Rosseland, *Zeit. f. Phys.* xiv. p. 173 (1923).

† The conditions necessary for the measurement of periods are discussed in the appendix to my 'Physics' (Camb. Univ. Press, 1920).

decreased indefinitely, the ratio  $n/m$  tends to a limit characteristic of the atoms A and B and the type of change in them observed. This proposition enables us to measure magnitudes having the properties associated with periods: but it is a purely statistical proposition, having no meaning as applied to individual atoms. The view that is suggested here is that all clocks are essentially similar to radioactive clocks and depend on similar statistical propositions.

The value of these ideas would be proved decisively if it were possible to produce a theory, involving no temporal conceptions other than time-order, which would reduce all quantum phenomena to a few simple principles and at the same time to show that all the experiments on which the prevailing temporal conceptions are based can be described adequately in terms of statistics. I make no pretence of being able to achieve this aim even approximately; and so long as it is not achieved, there is a certain difficulty in considering the ideas at all. Temporal conceptions are so deeply embedded in all our thoughts and language that, if we decided to abandon them entirely in discussing atomic phenomena, we should find that we could not even state adequately the problems we desire to solve. This is, of course, no objection to our theory, but a point in its favour; but a mere denial that certain questions which have troubled us are significant cannot be regarded as a complete solution of an inconsistency unless something positive is added to our thought to replace that subtracted from it. While the complete solution is lacking, it will be wiser to abandon all attempts at formal consistency, and to use temporal conceptions freely, even in circumstances in which their validity is denied, if by so doing we can hope to arrive at suggestions in what direction to seek the complete solution.

Thus, strictly speaking, we deny that there is such a thing as the interval between two successive transitions in a single individual system, or that there can be any meaning in a proposition asserting that any one such interval is equal to or greater than another. But it is more convenient, so long as we recognize the danger of misinterpretation, to admit the conception of the interval and the ideal possibility of measuring it, but to assert at the same time that this interval is wholly irregular, so that no law, other than a statistical law, can be asserted of it. With this preliminary explanation, let us turn to a few of the outstanding problems of quantum theory.

*Interaction of Rays with Atoms.*

The easiest to resolve is that which Bohr \* has indicated recently in connexion with the interaction between atoms and charged particles. The lack of "reciprocity" arises when the time that the interaction lasts is short compared with the period characteristic of the atom. The conclusion that it is short depends entirely on the assumption that the motion of the particle and the oscillation of the atom are "uniform." This, of course, we deny. Particles moving with "uniform" velocity or oscillating in fixed orbits are, in our view, undergoing fortuitous transitions between the points of their paths, the intervals between these transitions being wholly irregular, but possessing a statistical average related simply to the distance covered in the transition. Sometimes the time during which the atomic electron and the ray are near enough to interact is long, sometimes it is short; sometimes they will disturb each other much, sometimes very little. It follows that the only characteristic of an individual particle, inside or outside the atom, is its path, the locus of the points between which transitions occur; its velocity, its kinetic energy, the magnetic field it exerts are all statistical magnitudes, characteristic not of single particles at a single instant, but only of large aggregates of particles or (possibly) of a single atom observed at a large number of instants. And, as a matter of fact, the path of an individual ray is all that ever has been observed, or is likely to be observed. Unless we can measure, by the methods from which these quantities derive their meaning, times of the order of  $10^{-12}$  sec. or energies of the order of  $10^{-12}$  calories, no experiment can contradict our hypothesis.

*Radiation.*

But does it help us to overcome the great difficulty of radiation, and to reconcile the quantum and wave theories? Not, of course, without some modification of both, but the necessary modifications seem a natural consequence of it. At the outset we deny that radiation is periodic in time at all. We accept the direct experimental datum that atomic transitions result in the establishment of an electromagnetic field (by which we mean a modified probability of transition of atoms immersed in it) periodic in space about those atoms; but we deny the periodicity in time. As a consequence we can deny also the permanence of this field, for it no longer has to endure in order to produce its effect.

\* N. Bohr, *loc. cit.*



We suppose that the transition from a path of a higher to one of lower mean energy, which "emits radiation," establishes immediately round the atom the field periodic in space; an electron in the field at the lower level acquires an increased probability of transition to a higher and, in virtue of this probability, there is established around it a secondary field periodic in space (which it is natural to regard as opposite in sign to the first). The various secondary fields, superimposed on each other, interfere like Huyghens wavelets, and produce a periodicity on a larger scale which we detect by our instruments. As soon as the compensating transition takes place, after an interval and at a point determined by the probabilities established by the field, the fields vanish.

This picture is obviously similar to that of Bohr, Kramers, and Slater. But it has the advantage of not being disproved by the experiment of Bothe and Geiger\*. That experiment showed that the time-interval between the emitting transition and the consequent ionization of another atom is short compared with the average interval between successive ionizations. But this result raises a difficulty only if it is assumed that the radiation endures for the whole interval between successive ionizations. This we deny; all that the experiment proves for us is that the time for which the radiation endures is something less than  $1/1000$  sec.; it would clearly be surprising, in our view, if it lasted as long. Incidentally, it may be noted that we may get a very simple explanation (which never seems to me to be afforded satisfactorily by the classical theory) of why light from different sources does not interfere; it may be simply because the chance that the radiation fields from the two sources are actually present at the same time is infinitesimal.

It may be said that this is no explanation, for it involves the abandonment of the wave theory; in particular it leaves no room for a finite speed of propagation of light. The first part of this statement may be admitted, for any acceptance of quantum theory involves such abandonment. Maxwell's equations (one of which is a generalization of Ampère's law) apply in the first instance to material systems, made up of electrons moving in electric and magnetic fields, to which quantum principles must ultimately apply. Any argument which professes to deduce from these equations any proposition about a radiation continuous in time and space, and therefore outside those principles, must contain either a fallacy or a concealed assumption concerning the relation

\* W. Bothe and H. Geiger, *Zeit. f. Phys.* xxxii. p. 639 (1925).

between continuous and discontinuous phenomena. There is no inconsistency in combining a wave theory with the quantum theory, but there is inconsistency in asserting that this wave theory can be deduced from Maxwell's equations in their present form.

But the second objection cannot be admitted ; there is clearly room for an explanation, so long as the explanation is sought in the right direction, which is the opposite to the usual direction.

The quantity  $c$  enters into physics in two ways : first as the velocity of light, second as the ratio of a magnetic to an electric force. Maxwell's theory takes its second significance as fundamental, and seeks to explain the first. But relativity clearly tells us that we must reverse the process. The so-called velocity of light is the ultimate universal constant of all physics. It does not, of course, represent a velocity in our sense, that is to say the probability of transitions along a path ; it represents the invalidity of the conception of simultaneity for events which are separated in space. There is no such thing as the simultaneity of two events that are not neighbouring, and we must avoid that conception even in stating the facts from which we measure  $c$ . We must describe those facts by saying that if A is a transition associated with a transition B in a distant system in the manner of which the statistical representation is cause and effect, and if B is similarly associated with C in a system neighbouring to A, then C is not statistically simultaneous with A but is later \*, the statistical interval being proportional to the distance of A from B. That experimental fact we take as ultimate and inexplicable.

Now consider a particle moving in an orbit, or, as we say, undergoing transitions the locus of which is a closed curve. Each of these transitions is associated with that immediately preceding in the manner described ; and consequently, since the path is closed, a transition at P is associated, through an intermediate chain, with itself ; speaking conventionally, the stimulus returns on itself. If the path were infinitely small, the return stimulus would be statistically simultaneous with the outgoing stimulus ; but if the path is finite it will be later. The probability of a transition at any point, being determined partly by the return of the stimulus which the transition sets up, will thus be affected by the dimensions of the closed path. But the statement that the force on a particle is changed is the statistical representation of the

\* Or earlier ; the decision between the two alternatives depends on a mere convention concerning the sign of the causal relation.

assertion that the probability of its transitions is changed ; consequently the force on the particle (and the force which it exerts on other particles) will depend on the dimensions of the path and, probably, on the probability of transitions in it as compared with that in other paths of the same size. That is to say, the (electrostatic) force which the particle would exert and experience if it were not undergoing transitions will be modified by another (magnetic) force depending on the size and velocity of the orbit. Whether it is possible by any mathematical argument based on these ideas to establish the necessary relation between the form of the orbit, the statistical velocity, the quantity  $c$ , and the magnetic force is a matter on which I offer no opinion. But such an argument is physically conceivable.

### *Quantum Mechanics.*

Finally there is the problem of quantum mechanics. Does the conception of a statistical time enable us to understand better why stationary states are discrete and differ by finite amounts of energy, or how the energies characteristic of them depend on the constitution of the system? It is clear at once that a mere alteration of our ideas of time imposed upon classical theory will not explain everything ; the existence of the universal constant  $h$ , which is not a purely temporal constant, necessitates the introduction of some new ideas that are not temporal. The best that we can hope to do in explaining this constant is to exhibit a connexion between the two aspects under which  $h$  appears, determining first the stationary states that are possible and secondly the character of the radiation associated with transitions between them.

It seems to me that the views just discussed do help us to understand this connexion ; for we regard the stationary states as consisting of transitions just as much as the changes from one stationary state to another ; the only difference is that, while these changes consist of transitions between states of different mean energy, the stationary states consist of transitions between states of the same mean energy. If  $h$  is connected with one kind of transition, we should expect it also to be connected with the other. Further, on our view the periodic field which appears experimentally as radiation is not consequent on a transition between stationary states and separable from it, at least in conception ; it is simply the expression of the existence of a certain probability of transition. Planck's formula states a relation,

which must be regarded as ultimate and inexplicable, between the spatial periodicity of the field and the change of energy in the transition the probability of which is expressed by the field. In a stationary state, where there is no probability of change from that state, there is no probability of change of energy; the periodicity is infinite; the field is aperiodic. When there is a probability of a transition between stationary states with change of energy, the periodicity is finite; there is radiation. It must be clearly understood that the frequency of radiation, a temporal magnitude measured by the ratio of  $c$  to the wave-length, is not the statistical frequency determined by the probability of transition. The two are related in so far as the probability of transition is related to the energy change involved in the transition. In a single system the relation is doubtless unique, so that the frequency of radiation is a single-valued function of the statistical frequency of transition; but it is not impossible that in two different systems transitions could be found with the same probability and the same statistical frequency and yet of different energy change and therefore with different frequencies of radiation. The further study of the relation between frequency of radiation and statistical frequencies of transition (which, of course, is fundamental in Einstein's theory of complete radiation) seems highly desirable; for both these quantities are accessible to experiment.

These suggestions appear to be in accord, so far as accord is possible, with the quantum mechanics of Heisenberg and of Born and Jordan. For they, too, seem to regard stationary states as consisting of transitions. Their analysis depends on the use of double-affix quantities, such as  $\nu(mn)$ , which are associated with transitions, and in the formal treatment they make no essential distinction between quantities in which the affixes are different and those in which they are the same; but these latter can be associated only with transitions within the same stationary state. They actually represent the energy of a stationary state by a diagonal matrix with two similar affixes,  $H(mn)$ .

But this is as far as we can go in establishing a relation between our ideas and Heisenberg's theory; for there is a fundamental incompatibility between them. We are aiming at a physical interpretation, an interpretation in terms of concepts that are based as firmly as possible on experimental facts. Heisenberg's theory in its present form is not capable of any physical interpretation at all. It aims at deducing from a Hamiltonian equation of any form the energy of the

stationary states of a system to which that equation is applicable. But the very form of the deduction involves a denial that a Hamiltonian equation of any form is really applicable to the system; it denies the assumption, which underlies all classical dynamics, that the state of a system can be expressed by a series of one-one relations between space and time. To admit this is not to deny that the theory may be of great value; it may provide the best or the only mathematical analysis whereby certain physical truths can be revealed. And perhaps an inconsistency of this kind does not trouble mathematicians; indeed, a study of their excursions in relativity strongly suggests that it does not\*.

But the inconsistency must be removed before there can be any physical interpretation. It would be abolished if it were possible to dismiss altogether the conception of time, and start, not from a Hamiltonian equation involving time, but from a relation between the quantities which determine the constitution of a system to which, according to classical theory but not according to quantum theory, the Hamiltonian equation is applicable. In place of talking about a harmonic oscillator, we must talk about (*e.g.*) an electron inside a uniform positive sphere. Again, I do not profess to know whether the essentials of the Heisenberg calculus could be preserved in this change; but it is not inconceivable that they might be. For instance, we might still have the same formal equation on which the calculus is built—

$$\nu(mn) = \nu(mk) + \nu(kn);$$

but the  $\nu$ 's would now have a different physical significance. At present they are frequencies of radiation, and the difficulty arises at once that this equation, which states that frequencies are truly additive, like fundamental magnitudes, cannot be true generally of frequencies. Periods are, but frequencies are not, fundamental magnitudes in this sense. On the other

\* It is curious that they take it so lightly. For the prevalent school of mathematician-philosophers regard internal consistency as the prime criterion of truth. It seems that the deduction of conclusions which render insignificant the concepts of the premisses is an indication of falsity only if these concepts are purely mathematical; if they derive any part of their significance from sense-perception, the inconsistency does not matter. In simpler words, it is impossible to talk nonsense about what you know directly; and while you must not say that even numbers are odd, you are a true mathematician and display gloriously your freedom from the prejudices of the hide-bound physicist, if you assert firmly that black cats are white. I do not know that this doctrine has ever been formally maintained; I have merely deduced it from current practice.

hand, there are circumstances of great generality in which probabilities are additive, and others in which the logarithms of probabilities are additive. If, in the revised calculus, the  $\nu$ 's turned out to be probabilities or their logarithms, we might at once have a physical interpretation, and see an ultimate reason why mean energies are discrete and additive; and why the most fundamental proposition of quantum theory is true.

In conclusion, some apology seems to be needed for offering such a collection of incomplete and incoherent suggestions. If anyone can make any use of them he will be much better entitled than myself to be regarded as their author.

Feb. 18, 1926.

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C.I. *A Thermionic Valve Method of measuring the Velocity of Air-currents of Low Velocity in Pipes.* By J. A. C. TEEGAN, M.Sc.\*

[Plate XVIII.]

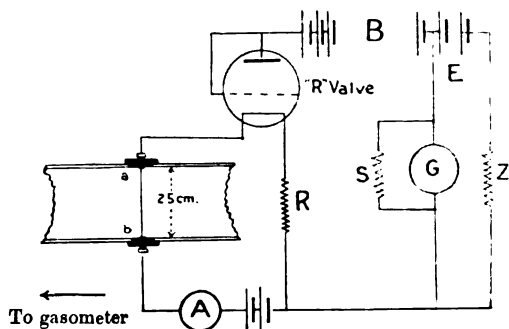
**T**HE fact that a fine platinum wire heated electrically undergoes a change in resistance due to cooling when immersed in a stream of fluid, has been utilized as a method of practical anemometry. Hot-wire anemometers based upon this principle have been described by Morris, and later by Thomas, who first applied them to the measurement of the velocity of fluids in pipes. The designs favoured by these workers resemble a bolometer arrangement, the cooling produced by a stream of fluid causing a change in resistance of a fine platinum wire which composes one arm of a Wheatstone bridge. In this paper a hot-wire anemometer of quite a new type is described, which has been found quite satisfactory for the measurement of slow-moving streams of air in pipes.

Into the filament circuit of an ordinary R-type thermionic valve a fine platinum wire (2.5 cm. long and 0.010 cm. diameter) was placed. This wire was stretched across a cylindrical tube 5 ft. long and 2.5 cm. diameter. The method of inserting the wire is indicated in fig. 1. The ends, *a*, *b*, of the wire were affixed by the smallest possible amount of solder to two brass screws fixed diametrically with respect to the section of the tube. Two stout insulated copper wires were attached to these screws, and were connected, as indicated, into the filament circuit of the valve, which also

\* Communicated by John J. Dowling, M.A., F.Inst.P.

contained a reliable ammeter A and rheostat R (fig. 1). The tube containing the platinum wire was clamped horizontally, and was securely connected by a pipe, of the same diameter, to a gasometer of 8 cubic feet capacity. The gasometer was fitted with ball-bearing pulleys, and its rate of fall was found to be exceedingly uniform, so that quite small air-streams could be produced and measured with accuracy.

Fig. 1.



When a stream of air cools the platinum wire, its resistance diminishes, and a greater p.d. is therefore applied to the valve filament. The resulting increase of filament temperature causes a corresponding increase in the current flowing in the anode circuit BG. The anode-current variations can be utilized as a measure of the velocity of the air-stream passing the wire. The grid and anode were joined and sufficient voltage applied for saturation. To enable a sensitive galvanometer to be used, a "zero-shunt" arrangement is employed. It is represented in fig. 1, and consists of a few cells E (6 volts) in series with a resistance Z, the whole being in parallel with the galvanometer G. If I is any value of the anode current, a current  $\frac{Z}{Z+G}(I-I_0)$

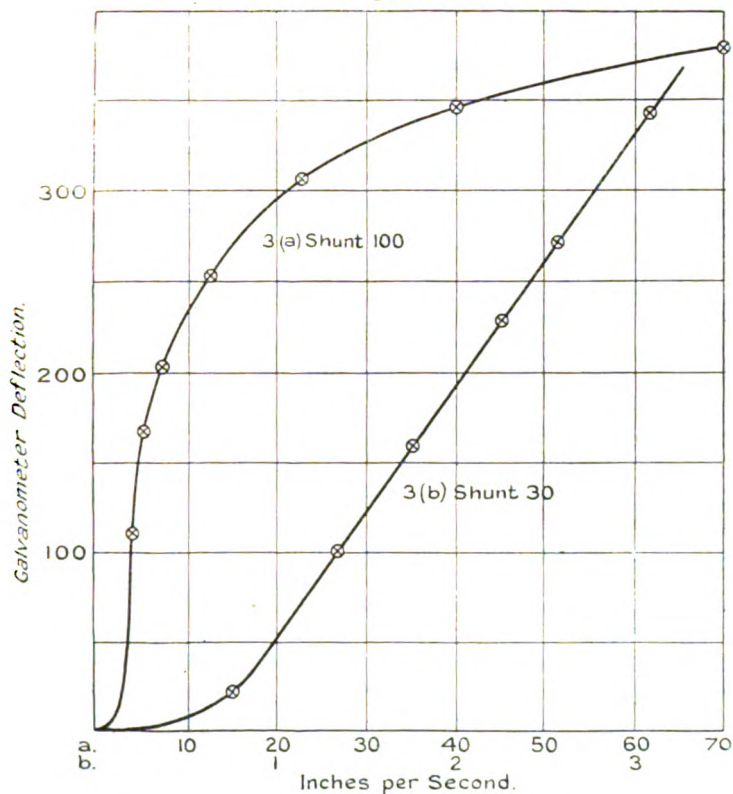
passes through the galvanometer branch, where  $I_0 = \frac{E}{Z}$  and

G is the galvanometer resistance. Thus, for valves of anode current in the neighbourhood of  $I_0$  a galvanometer of high sensitivity can be used to measure slight deviations from the standard value  $I_0$ . The galvanometer used in these experiments had a sensitivity of 300 scale-divisions per micro-amp.

In determining a suitable value of heating currents for the measurement of comparatively low velocities of flow,

the presence of the free convection current is of considerable importance. The wire being mounted horizontally, this convection current is at right angles to the cooling stream. The effective velocity of the cooling stream is  $\sqrt{V^2 + v_c^2}$ , where  $v_c$  is the velocity of the convection current, and  $V$  is that of the impressed air-stream. It is evident that  $v_c$  will diminish as  $V$  increases, since an increase in  $V$  lowers the temperature of the wire. If the diminution in  $v_c$  is proportional to  $V$  or to  $V^n$  (where  $n$  is a positive integer),

Fig. 2.



then the free convection current will have less influence on the form of the calibration curve the lower the heating current employed. A filament current of 0.6 amp. was used in this work, further reduction being found unsuitable, owing to the curvature of the valve emission curve commencing in the vicinity of a filament current of .55 amp.



## 1120 *Velocity of Air-currents of Low Velocity in Pipes.*

Fig. 2 (a) shows the relation between galvanometer deflexions and velocity of the air-stream (in inches per sec.). Over a range of velocities from  $\cdot 7$  inch per sec. to 5 inches per sec. the calibration curve is practically linear. The effect of the free convection current is clearly shown at the lower end of the curve. The sensitivity is quite good, equal to that obtained by other workers, and the readings are quite steady.

It was not generally possible to increase the sensitivity by lowering the galvanometer shunt ( $\times 30$ ) as the readings showed unsteadiness. It is possible that, with a better constructed flow-tube, in which sources of error due to cooling effects of the leads etc. were more completely eliminated, the sensitivity would be increased tenfold. In fig. 2 (b) the calibration curve for higher velocities is shown. It resembles that obtained by other workers.

Over a considerable range of velocities a fairly open scale of deflexions is obtained. As the velocity is increased, a point is reached where the curve turns over. The range could be extended to the higher velocities by increasing the temperature or diameter of the wire; using either a power value or a number of values in parallel. Since the anode current employed when using a valve in this way is large, it is necessary to use H.T. batteries of large capacity. A battery built up from a number of separate cells was found most satisfactory, the steadiness of the readings of the anemometer being very much improved.

An interesting test was made with this apparatus on the occasion of the second explosion test at La Courtine, the apparatus not having been ready in time for the first. The platinum wire was mounted in a short tube leading into an empty steel cylinder of about 80 litres capacity. A second galvanometer, in series with the first, recorded on a moving kinema film. The apparatus was run continuously for an hour covering the time at which the explosion wave might have been expected to arrive in Dublin. Plate XVIII. represents a portion of the resulting record, and the two large deflexions thereon were much larger than any other of the irregular galvanometer movements. We were informed by the Air Ministry, London, that the times indicated agreed pretty well with other long distance records obtained elsewhere.

CII. *Evidence of Molecular Changes in Vapours and Liquids.*

By G. N. ANTONOFF, D.Sc. (Manch.) \*.

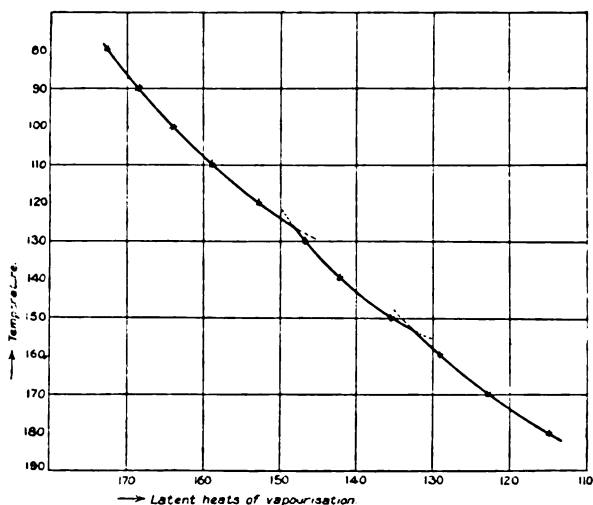
## I.

## INTRODUCTION.

IN my previous paper † I collected evidence indicating that some properties of liquids vary with temperature in a discontinuous manner. Thus, densities, latent heats of vaporization, surface-tensions, and viscosities were found to possess the above character.

The discontinuity of curves representing the variation of latent heat of vaporization with temperature is so conspicuous that one cannot help noticing the same (see fig. 1).

Fig. 1.



In some other cases it is by no means obvious at first sight, and it took me quite a long time to make sure that such is actually the case, and is not a result of imagination. The difficulty is that in most cases one has to deal with changes which do not exceed appreciably the limits of experimental errors. In the case of latent heats ( $\lambda$ ) of vaporization, as I said, the effect is much stronger, but it depends upon the

\* Communicated by the Author.

† Phil. Mag. vol. 1. p. 265, July 1925. In this paper I found a certain number of misprints particularly in the tables. For example, on p. 273 in the first line 1·63000 stands for 1·6300, and on p. 272 1·55470 stands for 1·55470; correspondingly on p. 275 first line, 663·0 should be instead of 66·30.

*Phil. Mag. S. 7. Vol. 1. No. 5. May 1926.*

4 C

measurement of densities, and therefore cannot be regarded as an independent evidence.

The figures I used were taken from the paper by Sydney Young (Proc. R. Dublin Soc. xii. June 1910), as calculated by Dr. J. E. Mills, by his formula

$$\lambda = \frac{K}{\sqrt[3]{d} - \sqrt[3]{D}},$$

where  $\lambda$  is the internal heat of vaporization, and  $d$  and  $D$  are densities of liquids and saturated vapour.

Similarly, if  $\lambda$  is calculated from the Clausius-Clapeyron formula

$$\lambda = T \frac{dP}{dT} (V - v),$$

where  $T$  is the temperature,  $V$  the specific vol. of vapour,  $v$  the specific vol. of liquid, and  $P$  the vapour-pressure, the discontinuity will be partly due to  $V$  and  $v$  (the reciprocal values of densities) and partly to  $P$ , which is apparently also discontinuous.

These data were of great service to me all the same, as they enabled me to locate the kinks without much labour, simply by plotting them on millimeter paper. However, I fully realize that all depends upon the density curves whether their discontinuity is beyond doubt.

Although the effect in question is small, there is no doubt that the measurements of densities can be carried out with much greater accuracy than those of most of the physical properties. The experimental figures are given with four decimal places, and the discontinuity can be noticed if only three figures are taken into consideration. Although in some individual cases there may be some doubt as to the actual position of a kink, in the majority of cases the results are quite definite.

In my previous paper I gave as an example the results for three substances of a very different chemical character, but I satisfied myself that the same is the case with all other substances for which there are accurate experimental values.

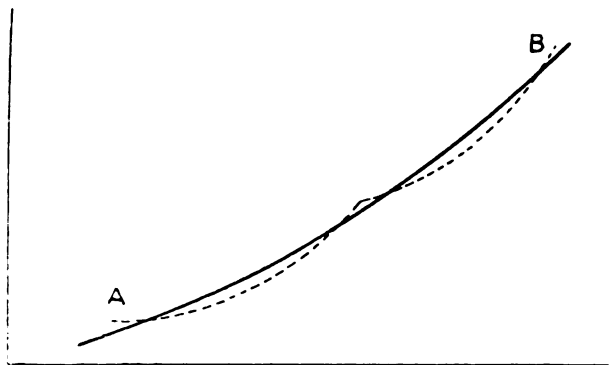
I have not investigated water owing to the want of figures at higher temperatures, and the behaviour of water near 4 C. is the only case so far where the laws outlined in my previous paper do not apply.

Thus, I have no doubt whatever that the above phenomena are real. However, since the publication of my last paper I have been in correspondence with a number of men of science, who criticized my work, and I find it therefore necessary to give some additional explanations.

Thus, for example, an opinion was expressed that such

formulae as I used for small portions of the density curves can be equally well applied with a sufficient degree of accuracy to a perfectly smooth and continuous curve. As my equations contain three constants they can be always adjusted so as to fit fairly accurately into separate portions of a perfectly continuous curve AB, as in fig. 2.

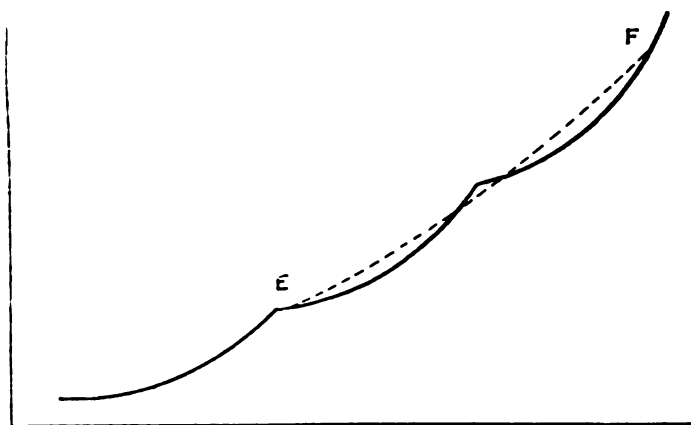
Fig. 2.



My answer to this criticism is as follows :—

If the curve were smooth, an approximate equation could be applied to any small part of the curve, between any two points. Experience has shown me, however, that such is not the case if the curve is discontinuous. Only those parts

Fig. 3.



of the density curves can be fitted accurately into an equation of a smooth curve, which are situated between two kinks.

Fig. 3 represents a density curve in an exaggerated form.

It can be seen that a part of the curve between E and F cannot be forced into an equation of a smooth curve.

It may be interesting to mention that I first discovered these kinks, not by noticing them on a drawing, but by finding that there are definite points on the curve between which only an equation of a smooth curve can be applied. Thus, I found that between these points an exponential expression can be applied with accuracy, the deviations being sometimes of the order  $\pm 0.0001$  or even less.

If, however, I try to apply an equation of a smooth curve between any other points (such as E and F in fig. 3), I find that the deviations become systematic, of a much greater order of magnitude than the above, and, in fact, only the points on which the curve is based will coincide accurately with the experimental results.

Only after these calculations revealed to me the existence of kinks, I plotted the figures on a piece of millimetre paper, on such a scale that 1 mm. corresponded to a unit in the third decimal place. With the use of a flexible steel curve, I drew the curve which revealed the kink on exactly the same places. Between these kinks, and only between them, an equation of a smooth curve could be fitted in accurately.

I thus found that the points nearest to the kink generally contain an appreciable error, which is probably due to interpolation, but apart from that I believe the experimental figures to be accurate within  $\pm 0.0001$ , on the whole, *i. e.*, within these limits they can be fitted into a smooth curve as a rule, at least in those regions where the experimental difficulties are not too great. It may be that the actual errors of observation were bigger, but the figures were smoothed afterwards. In such case a curve drawn on the basis of these figures is the best representative line.

In any case the experimental figures indicate the existence of quite a definite physical phenomenon, which cannot be attributed to experimental errors. I can quite imagine that in one case or two the experimental errors might be misleading and indicate the existence of purely imaginary relations, but the fact that these phenomena occur invariably with all liquids, at all temperatures, is a sufficient guarantee of their reality.

I am quite sure that kinks may appear much more distinctly under certain circumstances, and I can think of certain closely-related phenomena governed by precisely similar laws where one can succeed in finding them without much difficulty.

In my previous paper I mentioned that in dealing with

pure liquids I always bore in mind systems capable of separating into two liquid layers, which I generally call systems liquid-liquid, to distinguish them from systems liquid-vapour, *i.e.*, pure liquids in equilibrium with their vapour.

Comparing systems liquid-vapour with systems liquid-liquid, one cannot help noticing a striking similarity. Both systems have a typical critical point, with the typical phenomenon of opalescence in the critical region all round the critical point. In both cases the system separates into two phases of equal volume, in the critical point.

In both systems the meniscus separating the two phases in equilibrium is flat at the critical point and in its vicinity, etc.

The only difference is that in one case the one phase is liquid, the other gaseous, and in the other case both phases are liquid. With this reservation one cannot help seeing a striking resemblance between the two phenomena.

In this paper I shall treat these two categories of phenomena in parallel. By extending the analogy between them one can draw valuable conclusions because properties of one of them often reflect light upon the other. Of all physical properties I am particularly interested in densities and surface-tensions, and I shall deal with them in separate paragraphs. On the other side, I find that certain valuable conclusions as to the structure of liquids can be deduced from the study of conditions of equilibrium, and to this subject I devote two separate sections as well.

### § 1. *Densities.*

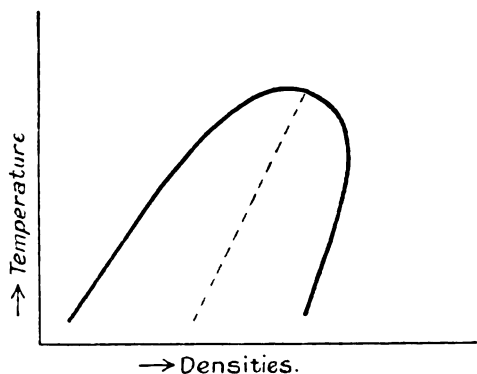
One of the striking examples of similarity between the two systems is the fact that they both follow, as a rule, the so-called Mathias-Cailletet law of rectilinear diameter.

Fig. 4 represents the densities of a liquid and its saturated vapours as a function of temperature.

This curve is, as a rule, of the shape of an asymmetric parabola. It is often observed that the values of  $\frac{\delta_l + \delta_v}{2}$  (where  $\delta$  is density of liquid, and  $\delta_v$  that of its vapour) fall into a straight line. The intersection of this line with the parabola indicates the position of the critical point. Every horizontal line intersects the two branches of the parabola in points which represent the density of liquid and of its vapour at the given temperature. In my previous paper I dealt with this subject in brief, and there I gave reasons

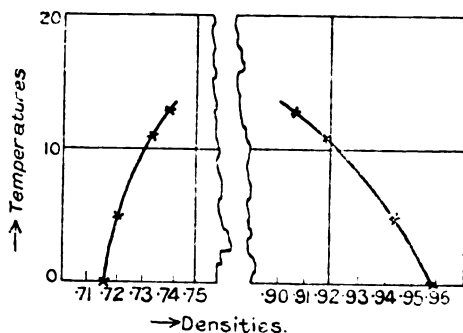
why I believe that this parabola is discontinuous, although to a very small degree. The general character of the curve is such that it certainly does not suggest the idea of discontinuity. Only a very careful examination can reveal it, and even then it is difficult to convince other people who have not gone through the amount of work I have. The effect is so small that it is only slightly above the limits of experimental errors.

Fig. 4.



The same can be said about systems liquid-liquid. I have determined experimentally the densities of coexisting liquid layers for the system aniline-amylene, at different temperatures. (See fig. 5.) The curve appears to be very nearly smooth.

Fig. 5.



In the systems capable of separating into two layers the relation between the specific weights and concentration is by no means simple.

Thus, for aniline and amylene, at  $19^{\circ}3$  C., *i. e.* about  $5^{\circ}$

above their critical point of dissolution, I found the relation as represented in fig. 6.

Fig. 6.

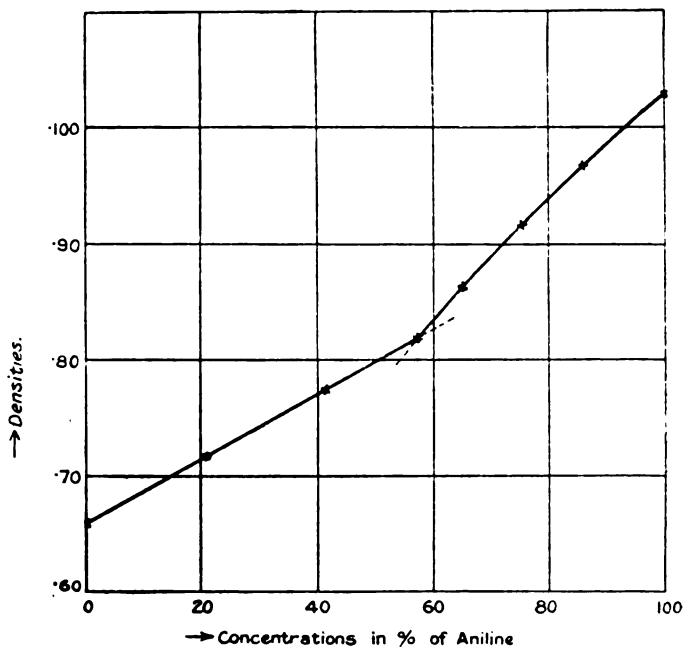


Fig. 7.

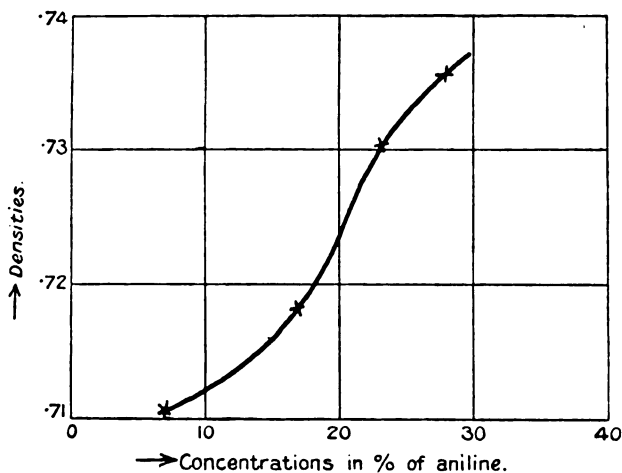


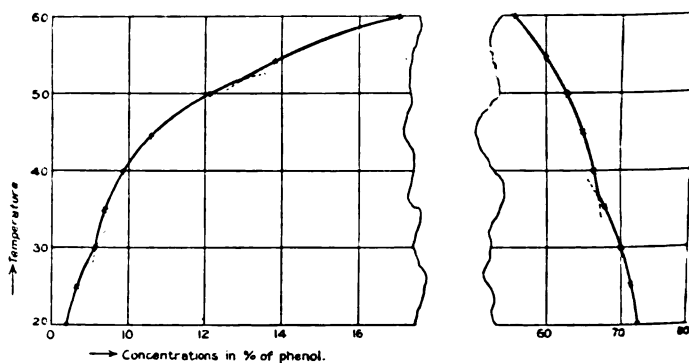
Fig. 7 shows the relation between the densities and concentrations for saturated solutions of the same system



between  $0^{\circ}$  and  $20^{\circ}$  C. for the upper layer, *i. e.* for the branch on the right-hand side in fig. 5. The relation for the other layer is substantially of the same character.

It is obvious that the asymmetric parabola with densities plotted as abscissæ, being very nearly smooth, must become strongly discontinuous if concentrations are plotted instead of densities. See fig. 8, which represents the data for the system phenol-water, taken from the Landolt Börnstein Tables, where there are many similar examples of the same kind.

Fig. 8.



It is noteworthy that by plotting the excess of concentration of one layer compared with the other, a strongly discontinuous curve is obtained which is represented in fig. 9.

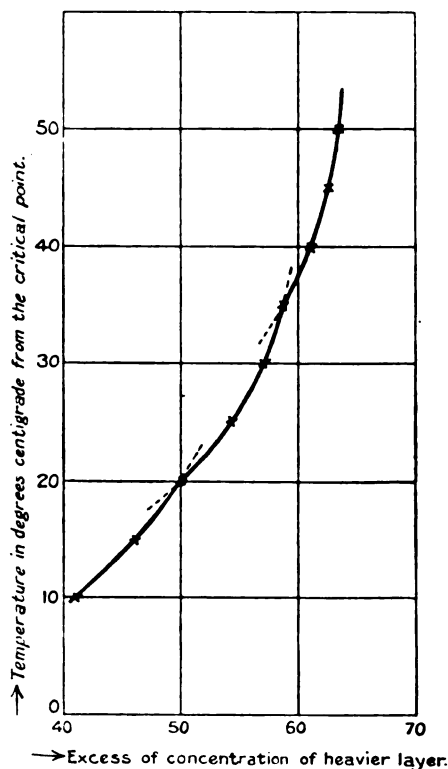
It is similar in character to the  $\delta$ -temperature curves dealt with in my previous paper (where  $\delta$  is the difference between the density of liquid and its vapour), but its discontinuity is much more pronounced.

By plotting  $d$  (the difference of densities of two saturated liquid layers) against temperatures, I obtained a curve of the same character as the  $\delta$ -curve. It also follows the horizontal axis very closely, starting from the critical point, and its equation must be also of the form

$$Ae^{\lambda d} = T + A.$$

It thus appears that the discontinuity is an intrinsic property of liquid systems. By plotting densities against temperatures the discontinuity is partially compensated, but it is still there.

Fig. 9.



## § 2. Interfacial Tension.

It is also interesting to follow up the similarity between the systems liquid-vapour and liquid-liquid from the point of view of surface-tension.

By comparing the two classes of phenomena, one cannot help noticing the following:—

When a system liquid-liquid is cooled just below the critical point at which a homogeneous solution separates into two liquid layers, the meniscus between the two layers is flat. I have photographed the same in the vicinity of the critical point with considerable magnification, and I found that even at a certain distance from the critical point it remains very nearly flat. The measurement of interfacial tension in these regions often presents great difficulties, and for this reason I determined the surface-tensions of both coexisting layers separately. I found that even at a certain

distance from the critical point both the layers have practically equal surface-tension, or at least no appreciable difference can be detected by the capillary method. This is a sequel of a general law for the whole critical region all round the critical point, that the surface-tension is independent of concentration in this region. In other words, the interfacial tension  $\alpha_{12}$  is very nearly  $=0$ , and the curve representing the change of  $\alpha_{12}$  with temperature from the critical point follows very closely the axis of temperatures, and its equation must be of the form

$$\alpha_{12} + A = Ae^{\lambda T}.$$

Now, in systems liquid-vapour, when the critical point is reached and the meniscus appears in the middle of the tube, one cannot help noticing that the meniscus is flat. The rise of the liquid in a capillary tube becomes appreciable only at a certain distance from the critical point. At the critical point, or in the immediate vicinity of it, the capillary rise is not detectable experimentally, and some authors even observed a slight capillary depression and not rise, although this was afterwards attributed to the experimental errors\*.

Anyway the surface-tension  $\alpha$  is very small at the start from the critical point, it follows very closely the temperature axis, and, as shown in my previous paper, its equation is

$$\alpha + A = Ae^{\lambda T}.$$

The fact that the meniscus at the critical point is flat is very significant. *It means that the gaseous phase has surface-tension equal to that of the liquid phase.* We have no method of measuring the surface-tension of the vapour, nor of that of a liquid. What we really do is to measure the tension at the interface between liquid and vapour which is equal to the difference of surface-tensions of the two coexisting phases.

In this sense what we call surface-tension  $\alpha$  in systems liquid-vapour is an analogue of the interfacial tension in systems liquid-liquid. The fact that the interfacial tension remains negligible even at some distance below the critical point indicates that in these systems the surface-tension is also independent of concentration. It is therefore reasonable to conclude that such will also be the case above the critical point.

The same applies to the normal pressures. The normal pressure of both phases is the same at the critical point and

\* Wolf, *Ann. de Ch. et Phys.* (3) xlix. p. 270 (1857); Drion, *ibid.* (3) lvi. p. 221 (1859); Clark, *Phil. Mag.* (5) x. p. 145 (1880).

in its immediate vicinity. At lower temperatures their difference becomes more and more appreciable.

This subject will be further discussed in the section on conditions of equilibrium.

## II.

### CONDITIONS OF EQUILIBRIUM.

To define conditions of equilibrium between two coexisting phases, I shall treat the systems liquid-liquid in the first place.

It is quite natural to ask oneself the question: Why do they not mix on shaking? One would expect that the greater the difference of concentration, the greater must be their tendency to mix.

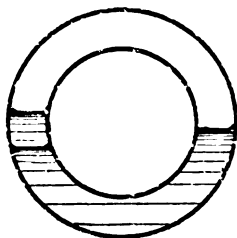
And yet the experimental evidence tells us that quite a number of physical properties in the systems of that kind remain constant with the increase of concentration. And particularly such properties as depend upon the number of molecules and not their nature.

#### *Vapour-Pressure.*

Thus, *for example, the vapour-pressures are independent of concentrations, even well outside the solubility curve* in the regions of an unlimited mutual solubility\*. The depression of vapour-pressure in a solution is proportional to the number of molecules dissolved (Raoult's law).

The two liquids in equilibrium must have the same pressure and composition of vapour (Konovalov's law), because otherwise there can be no equilibrium.

Fig. 10.



Imagine an annular ring, as shown in fig. 10, containing two layers in equilibrium. If both layers did not have the same vapour-pressure there would be a continuous distillation—a kind of perpetual motion.

\* See D. Konovalov, *Ann. d. Phys.* x. p. 315 (1903).

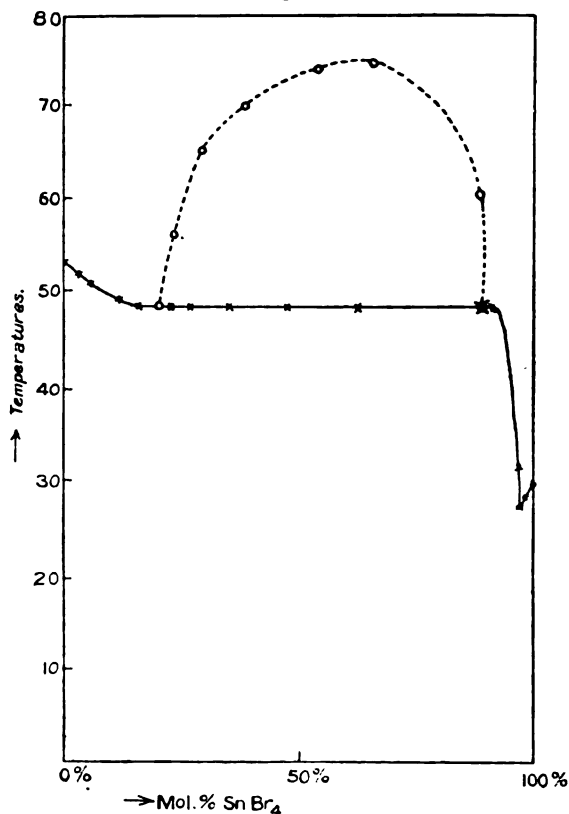
Thus the above law is in accordance with the laws of thermodynamics.

But the above considerations do not tell us how to reconcile Konovalov's law with Raoult's law.

### *Freezing Temperature.*

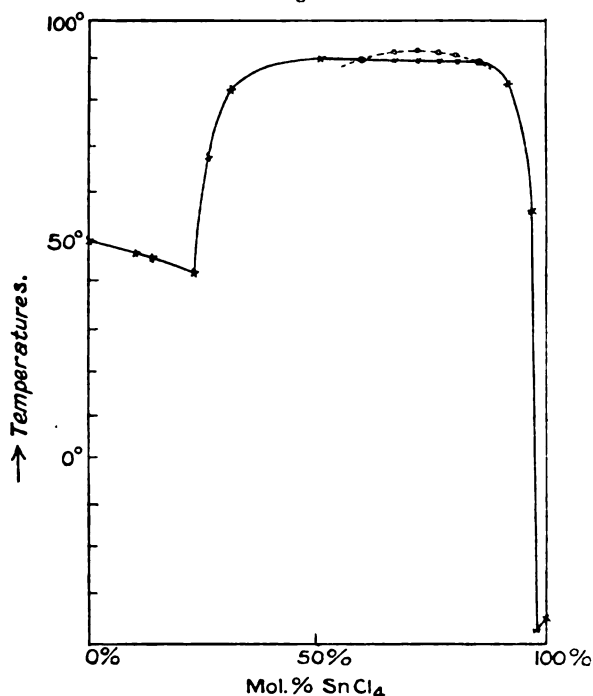
The study of freezing-point curves shows that the *freezing temperature is also independent of concentration within certain limits.*

Fig. 11.



I chose for this purpose two systems, viz. methyl oxalate and stannic bromide, and methyl oxalate and stannic chloride. The two pairs just reproduce experimentally the two possible cases, which were demonstrated by two rough diagrams in my paper (Phil. Mag. xxxvi. Nov. 1918, p. 394).

Fig. 12.



These results are represented in figs. 11 and 12, and the experimental figures given in the following tables.

TABLE I.  
Methyl-Oxalate—Stannic Bromide.  
*Solubility data.*

Mol. per cent. of SnBr <sub>4</sub> .	Temperature.	Mol. per cent. of SnBr <sub>4</sub> .	Temperature.
20.0	49°·2	65.4	73°·3
29.2	52°·6	90.1	61°·5
37.0	69°·8	90.5	49°·2
54.4	74°·9		

In this table temperatures are given at which solutions of a given composition begin to separate into two phases.

TABLE II.  
Methyl-Oxalate—Stannic Bromide.

Mol. per cent. of $\text{SnBr}_4$ .	Freezing Temperature.	Mol. per cent. of $\text{SnBr}_4$ .	Freezing Temperature.
0	<u>53.2</u>	54.4	49.2
.97	<u>52.7</u>	65.4	49.2
2.4	<u>52.3</u>	90.1	49.2
7.1	50.7	90.5	49.2
13.0	49.7	92.0	49.2
16.2	49.2	97.0	<u>31.0</u>
20.0	49.2	97.8	<u>27.8</u>
22.8	49.2	99.1	<u>28.4</u>
29.2	49.2	100	<u>29.0</u>
37.0	49.2		

TABLE III.  
Methyl-Oxalate—Stannic Chloride.

Mol. per cent. of $\text{SnCl}_4$ .	Freezing Temperature.	Mol. per cent. of $\text{SnCl}_4$ .	Freezing Temperature.
0	53.2	71.3	92
11.9	48.0	75.3	92
13.6	47.0	80.4	92
20.2	45	80.7	92
25.1	69	85.0	93
31.1	86	91.2	86
50.3	92	98.0	60
59.7	92	99.5	<u>-33.2</u>
68.1	92	100	<u>-32.2</u>

The solubility data could not be determined accurately because of instability of this system just in the region of

partial solubility. They are comprised between about 94 and 92° C. and are shown by a dotted curve in fig. 12.

The figures were obtained by observing the temperature at which the solid phase disappears in a solution of a definite concentration sealed in a glass tube, and subjected to energetic shaking in a bath of a suitable transparent liquid. The underlined figures were obtained by a cryoscopic method.

Both curves show that on addition of one of the components the freezing-point *curve becomes very nearly horizontal even outside the limits of solubility, and the two layers have the same freezing-point.*

The latter fact has already been mentioned in my paper of 1918 (*loc. cit.*). There I expressed the view that both solutions must be regarded as solutions in the same solvent, as they are situated on one side of the eutectic point as in fig. 11, or between two eutectic points as in fig. 12. In the latter case there is an evidence of a definite combination between the components of the solution, separable in crystalline form. It thus appears that we have to deal with a solvent of a somewhat complex nature. Both the saturated layers must be regarded as solutions in this solvent.

The fact that two layers in equilibrium freeze at the same temperature is likewise in agreement with the laws of thermodynamics, but it is in apparent contradiction with Raoult's law, according to which the depression of freezing-point is proportional to the number of molecules dissolved.

### *Boiling Temperatures.*

There is a similar law concerning boiling temperatures often known as Beckmann's law, stating that the increase in the boiling temperature is proportional to the number of molecules dissolved. Like the two other properties previously discussed, the boiling temperature always remains constant and the same for both layers in equilibrium.

### *Interpretation of the above results.*

Now I shall discuss these phenomena in the light of Raoult's law.

According to this law the lowering of freezing-point or vapour-pressure is proportional to the number of molecules dissolved in a given solvent. The lowering of freezing-point or vapour-pressure in the same solvent produced by equimolecular quantities of different substances is the same.

This law is said to be applicable to the very dilute solutions, in other words, those which must behave like

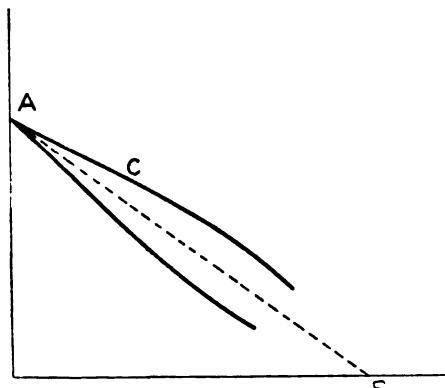


perfect gases. In practice this law is never strictly obeyed. Instead of proceeding along the straight line AB, fig. 13, the curve generally departs from it with the increase of concentration one way or another. That is why for determination of molecular weight of the dissolved body very dilute concentrations are generally used.

However, the liquids do not behave like gases, and according to my theory the change of temperature is always accompanied by a certain change in the molecular state. The results discussed in this paper suggest that in solutions the change of concentration may cause a similar effect—due to the interaction of the molecules. It thus appears that the very fact of change of temperature and concentration is one of the reasons why Raoult's law should not be obeyed in its pure form.

I thus find that to reconcile the laws of Raoult (and Beckmann respectively) with the above experimental facts,

Fig. 13.



it is necessary to make a special hypothesis as to the molecular state of dissolved particles in solutions.

I assume that, in all those regions where the properties mentioned do not change with concentration, the particles added combine with some particles in solution without increasing the number of particles dissolved.

Such an hypothesis does away with all difficulties in understanding these phenomena, and it is in agreement with evidence of quite a different nature, as will be shown shortly.

At this moment it is necessary to add that the above interpretation will be disputed by some people on the ground that Raoult's law and the like are only valid in the region of very low concentration.

Fig. 13 shows how the above properties change with

concentration according to Raoult's law (the straight line), and how they depart from it in practice one way or another.

These deviations may be also due to the same causes as the deviations from Boyle's law in gaseous systems. But for the object of this work it is sufficient to mention one possible case.

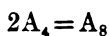
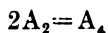
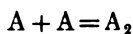
Take a certain point C on the diagram fig. 13 which has departed from the straight line appreciably. Suppose that at this stage the newly added molecules of the component begin to combine with some molecules in solution without increasing their number. We can then expect that the property will not change any more with the increase of concentration and the curve will become horizontal (not as is shown in fig. 13) for a certain range of concentrations.

If the number of molecules remains the same and the molecular field exercised by the new molecules is not substantially changed, we may expect that the surface-tension will be also independent of concentration, and such is actually the case in the critical region.

If these deviations from the simple laws were only due to such attractions as assumed by van der Waals, the surface-tension ought to increase with the increase of concentration. The increased concentration in such case means a larger number of molecules at a smaller distance, when the molecular forces become much greater.

I thus arrived at the conclusion that, in order to produce a system capable of separating into two layers, it is necessary that the number of molecules in solution remain unaltered with the increase of concentration. This condition, however, is not sufficient, because we saw instances of it in regions outside the boundaries of limited solubility. Apparently the separation into two layers does not take place until the molecular complex is present in a certain quantity.

As I said, both temperature and concentration may stimulate the formation of these complexes in several stages, such as



and so on.

It will be shown later on that, in accordance with the existing evidence, the above scheme represents molecular changes taking place in the system phenol-water.

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4 D

*Systems Liquid-Vapour.*

Now, let us see how far the above considerations can be extended over systems liquid-vapour. In this case such properties as freezing temperature and boiling temperature are of no use to us.

However, the relation between volume, *i. e.* concentration, and pressure in the critical region liquid-vapour is very significant. It is well known that well outside the limits of a symmetric parabola (within which the two phases coexist) the pressure remains very nearly independent of volume, *i. e.*, concentration.

It thus appears that there is a tendency in these systems as well to form complex molecules above, and all round the critical point. Changes of both temperature and concentration seem to favour their formation, and apparently the separation into two phases takes place when these properties reach a certain value.

This process is discontinuous, consisting of a series of distinct stages. Speaking only very roughly, one can describe the process of liquefaction as indicating continuity between the two states.

Thus, all facts mentioned in this paper show that the essential condition of equilibrium between two phases is a definite relation between the number of molecules in the two phases.

In the following section I will show that important conclusions of the same nature can be derived from consideration of conditions at the interface, which are necessary for the maintenance of equilibrium.

## III.

THE LAW OF DIFFERENCE AS A CONDITION OF  
EQUILIBRIUM AND ITS CONSEQUENCES.

In the preceding section certain physical properties were discussed with the view of specifying the conditions of equilibrium between two coexisting phases.

All the above data pointed to the fact that for the stable equilibrium it is necessary that the two phases should contain an equal number of molecules per unit volume.

It has been shown in my paper of 1918 that some considerations of a totally different nature lead to the same result.

Long ago I found that if the two saturated layers are in a state of equilibrium, the conditions

$$\alpha_{12} = \alpha_1 - \alpha_2$$

must be fulfilled, which I shall call for simplicity *the law of*

*difference.* I tried many times to prove the truth of the above equation as a condition of equilibrium from energy consideration.

If it is easy to show the truth of Konovalov's law (the equality of vapour-pressure) by means of a scheme shown in fig. 10, no considerations of that kind seemed to throw any light on the law of difference. I very soon came to the conclusion that no further step could be made in the matter unless something more definite is known about the structure of atoms and molecules, and the nature of the field of force exercised by them. This was the reason why I temporarily gave up work on these lines and began to work in what may appear at first sight a totally different domain—radioactivity. The development of this subject already then indicated that it would lead to a more intimate knowledge of the structure of matter.

When Rutherford published his theory of the atom (1911), I immediately felt that it was an impetus for the work I was interested in. I then went to Cambridge and devoted there most of my time to the development of the theory of surface-tension as a result of electrical and magnetic attractions exercised by electrical matter. This theory was ready in 1914 but its publication was delayed by the War, and it first appeared in 1918 (Phil. Mag. vol. xxxvi. Nov. 1918). In this paper I deduce the law of difference from relations connecting the normal pressure and surface-tension, on page 388.

It was shown there that this law could be deduced subject to the condition that the two phases in equilibrium contain an equal number of molecules per unit volume.

Now, we saw that there is strong evidence indicating that in systems liquid-vapour the conditions at the interface are subject to exactly the same laws—namely, the flat meniscus in the critical region means that the vapour and liquid have equal surface-tensions. This, together with the fact that the capillary rise in this region is very nearly = 0, is an indication that the law of difference must hold true also for systems liquid-vapour, so that

$$\alpha = \alpha_l - \alpha_v,$$

where  $\alpha_l$  is surface-tension of liquid and  $\alpha_v$  is surface-tension of vapour.

Assuming that  $\alpha_v$  is probably very small at lower temperatures,  $\alpha$  is practically the value of surface-tension of a liquid at low temperatures.

It is also natural to assume that the equation

$$P = P_l - P_v,$$

where  $P_l$  is the normal pressure of the liquid and  $P_v$  is the normal pressure of the vapour, must hold true.

Following the same arguments as before, I can put

$$P_l = k\alpha_l n_l^{1/3},$$

where  $n_l$  is the number of molecules per unit volume in the liquid

$$P_v = k\alpha_v n_v^{1/3},$$

where  $n_v$  is the number of molecules per unit volume in the vapour.

$$\therefore P = k(\alpha_l n_l^{1/3} - \alpha_v n_v^{1/3}). \quad . \quad . \quad . \quad (1)$$

On the other side the relation between  $P$  and  $\alpha$  must be of the form

$$P = k\alpha n^{1/3}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The equation (2) has a definite physical meaning and is compatible with (1), if

$$n_l = n_v = n,$$

*i. e.*, in a state of equilibrium there must be on either side of the interface separating the two phases an equal number of rows of molecules, each row containing the same number of molecules.

In other words

$$n_l = \frac{\delta_l}{Mx} = n_v = \frac{\delta_v}{My},$$

where  $\delta_l$  is the density of liquid,  $\delta_v$  that of vapour,  $M$  the molecular weight corresponding to a simple, non-associated molecule, and  $x$  and  $y$  association factors for liquid and vapour.

The above is a condition of equilibrium. It could not be deduced thermodynamically, because it involves a definite structural change, of which thermodynamics take no cognisance.

Thus, from the point of view of conditions of equilibrium, we arrive at a very important conclusion as to the molecular state of liquids at all temperatures.

Assuming that the vapour is monomolecular, *i. e.*,  $y = 1$ , 2

$$x = \frac{\delta_l}{\delta_v}.$$

Thus, the association factor is the ratio of density of liquid to that of its saturated vapour, if the vapour is monomolecular.

I shall try now to estimate  $x$  at temperatures corresponding to the kinks in the  $\delta$  curve, as indicated in my paper of July 1925.

It should be pointed out that the figures are not accurate enough in order to see whether a kink always corresponds to a whole number of  $x$ . I leave out of consideration the question whether it is so or not, and shall only add that I do not attribute to it much importance. Experience has shown me more than once that the position of kinks indicated by different physical properties, owing to a common cause, varies as a rule, and does not coincide exactly with places corresponding to definite molecular proportions.

I thus estimate that from the critical point  $x$  acquires the following values near the kinks for ethyl acetate :—

2, 6, 18, 36, 144, 864, etc.

The latter figure corresponds to a temperature of about 50° C.

It is seen that, according to this theory, the degree of association at low temperatures must be fairly high.

Following the same arguments I deduced the scheme for phenol-water. In my paper of 1918, describing the law of difference for systems liquid-liquid I used the letter  $p$  for the number of molecules per unit volume, where  $p$  meant the total number of molecules per unit volume, including the solvent. The number of molecules dissolved ( $n_1$  and  $n_2$ ) must be also the same for both layers per unit volume. In this case it is more convenient (for reasons which will be explained in the subsequent paper) to express the same in terms of concentrations ( $C_1$  and  $C_2$ ),

$$n_1 = \frac{C_1}{M_x} = n_2 = \frac{C_2}{M_y}.$$

By determining the ratios  $\frac{C_2}{C_1}$  corresponding to the kinks in the curve fig. 9, the scheme  $p$  (1137) is arrived at.

#### IV.

#### CONCLUSION.

The often observed departures from the laws of simple proportionality in vapours and liquids, such as Boyle's law, etc., have naturally resulted in many attempts to account for them.

Amongst these theories, perhaps the most prominent position is occupied by that of van der Waals. His fundamental idea is that the deviations from Boyle's law are due to the molecular field round the molecules, which causes attraction between molecules when they are brought close together owing to external pressure. The resultant of these forces causes a diminution of pressure exercised by a given volume of gas. This inward force per unit area is called normal or molecular pressure. Its presence also necessitates the existence of a force tangential to the surface. This force per unit length is surface-tension.

Although we may have no method of directly measuring the same, the surface-tension of vapours and gases may be sometimes quite appreciable.

In this sense one cannot help recognising the value of van der Waals's theory, as having explained the necessity for surface-tension and normal pressure in gases, although in its quantitative side it often fails.

On the other hand, the old theory of de Heen, which has not received general recognition, and may be practically regarded as abandoned, undoubtedly contains an element of truth. It failed chiefly owing to the want of experimental data in those days on which it could be tested.

I started my work without having any definite views of any kind.

Only after I followed up the analogy between systems liquid-liquid and liquid-gas, which, I believe, are governed by identical laws, have I formed a theory of my own.

I have come to the conclusion that the molecular field cannot account for the peculiar behaviour of isotherms in the critical regions, where, as has been mentioned before, a number of physical properties are independent of concentration. Some of them are very nearly identical for the two coexisting phases in the critical region only, and some are the same so long as the two phases coexist.

Thus I found experimentally that in the systems liquid-liquid the surface-tension does not vary with concentration above the critical point in the region of complete mixability.

According to my theory it means that in the expression for surface-tension  $\alpha$  (see *Phil. Mag.* xxxvi, p. 382, 1918).

$$\alpha = k l^2 p^{5/3},$$

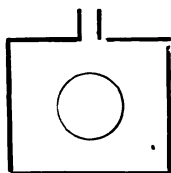
where  $l$  is the length of the doublet, and  $p = \frac{\delta}{\bar{M}}$  is the number of molecules per unit vol.,  $p$  remains constant with the change of concentration, *i. e.*, the molecules added combine with molecules in solution, so that their number remains

the same. And it also means that the molecules formed have the same  $l$ .

This is very nearly true for two phases in equilibrium in the critical region. At lower temperatures the surface-tensions of two phases begin to differ appreciably, and yet their other properties remain the same, viz., those which indicate that the number of molecules per unit vol. is still the same in both. Therefore, in this case, the newly-formed molecules in one phase have a bigger  $l$  than in the other, and yet one can see no effect of it on other properties.

I therefore conclude that Raoult's law has nothing to do with the magnitude of the molecular field, and that the deviations from it are due to some other causes.

Thus, although I believe in the surface-tension and normal pressure of gases, I do not believe the peculiar character of isotherms in the critical regions is due to this.



I should like to illustrate the above by the following model. Imagine a rubber ball with a fairly thick wall filled with air, whose pressure can be reduced by some means, or the pressure outside it increased, which practically amounts to the same.

There will be a certain tension and normal pressure in the membrane to counter-balance the excess of external pressure. Such a system, however, is not stable, and can exist only in more or less ideal conditions. A slight disturbance will do away with the stress in the membrane, or at least part of it, and a more stable equilibrium will establish itself with diminution of volume. If, however, the ball is filled with a liquid, the external pressure will cause stress in the rubber ball, and it will increase with the external pressure.

Similarly, in systems we are interested in, the increase of concentration probably could be followed by the increase in normal pressure, if the molecules were all alike and travelled with the same velocities. But as their velocities vary within certain limits, and the field is not uniform, it is quite probable that the molecules with velocities below the average will combine as a result of increased concentration, and thereby render the system more stable.

In such a case the normal pressure will not necessarily increase with concentration, but may remain substantially the same if the doublet of combined molecules does not differ much from that of a single molecule.

• In regions of high concentrations (which may be compared with the rubber ball filled with a fluid with small compressi-



bility), where the particles are close together, the molecular field will make itself felt with the increase of concentration.

I thus share the view of van der Waals so far, that I believe in a molecular field and its effect on certain properties of a system, but I do not believe the properties of critical regions are due to it.

All these phenomena can only be explained by the theory of molecular interaction.

In each of my previous papers I deal with phenomena of a widely different nature, and yet they all point to one and the same thing—the formation of complex molecules. Thus the changes of state must be invariably accompanied by the change in molecular complexity, and the formation of complex molecules begins above the critical point.

My theory also leads to the conclusion that all liquids must be highly associated at low temperatures.

It thus appears that according to the formula

$$P = k \alpha p^{1/3} \text{ (Phil. Mag. xxxvi. p. 312, 1918)}$$

connecting normal pressure, surface-tension, and the number of molecules per unit volume, one must expect a much lower value for the normal pressure of liquids at low temperatures than usually expected.

It would also mean that, if these phenomena of association remain in force in the solid state, one would expect much lower figures for the breaking stress than expected from electrical theory (which does not take into account the association and deals with single molecules), which is actually the case.

#### SUMMARY.

(1) It is shown in this paper that the systems liquid-liquid (*i. e.*, those which separate into two liquid layers) and systems liquid-gas are governed by identical laws.

(2) Thus it is shown that the temperature changes in systems liquid-liquid also take place in a discontinuous manner; the discontinuous character appears very strongly if concentrations of two saturated layers are plotted against temperatures instead of densities. It appears that both temperature and concentration changes favour the formation of complex molecules.

(3) The properties depending upon the number of molecules and not their nature, indicate that the number of molecules per unit volume remains the same with the increase of concentration in the critical regions and sometimes

outside them. The formation of complexes is a necessary condition for separation into two phases.

(4) The analogy between the two systems was extended to the conditions at the interface separating two phases. It was thus assumed that the law of difference must hold true for systems liquid-gas, with its natural consequence

$$n_l = n_v,$$

i. e., the number of molecules per unit volume in liquid is equal to the number of molecules in vapour. Or

$$\frac{\delta_l}{Mx} = \frac{\delta_v}{My}$$

where  $\delta_l$  and  $\delta_v$  are densities of liquid and vapour,  $M$  the molecular weight, and  $x$  the association factor of liquid, and  $y$  that of vapour.

(5) It is thus possible to calculate the association factor at all temperatures and to see that its value becomes fairly high at lower temperatures.

(6) In both systems one can recognize definite molecular changes. The difference between systems liquid-liquid and liquid-gas is that in the latter case these changes take place between molecules in a space not otherwise filled, whereas in the former they take place within a liquid acting as dissolvent.

The subject will be treated more fully in the subsequent paper.

### CIII. *Dimensional Analysis.* By NORMAN CAMPBELL, *Sc.D.*\*

#### SUMMARY.

A consideration of Mrs. Ehrenfest-Afanassjewa's principle of similitude. Her conclusion that results can be based only on a full knowledge of the laws determining the behaviour of the system is welcomed; but it is argued that her representation of the argument as primarily mathematical is misleading. The mathematical arguments involved are so simple as not to be worth stating; all the difficulties are physical. Any suggestion that results can be obtained by juggling with symbols and neglecting entirely the physical relations involved can only give fresh life to the fallacies of "dimensional analysis."

MRS. EHRENFEST-AFANASSJEWА says that the object of her paper is to promote agreement among writers on this

\* Communicated by the Author.



the factor of proportionality is different, although the same units are employed. Different systems involving a particle moving according to a law of the same form are characterized by different numerical values of  $f$ ;  $f$  is a magnitude capable of different values. In this it resembles  $s$  and  $t$ ; but it differs from them because, while  $s$  and  $t$  can be measured without any reference to numerical law, the measurement of  $f$  depends wholly on the truth of the law (1). Any physically significant statement about  $f$  implies that truth of (1); to say that a statement is characterized by an acceleration is precisely the same thing as to say that it is characterized by some particle moving according to (1).

We are now presented with a number of systems of which we are informed that each is characterized by a period  $T$ , a length  $S$ , and an acceleration  $F$ , each of these quantities being completely determined by the other two. We ask whether, and if so why, it is legitimate to conclude that, if the suffixes refer to different systems,

$$\frac{S_m}{S_n} = \frac{F_m T_m^2}{F_n T_n^2} \cdot \cdot \cdot \cdot \cdot \cdot (2)$$

The answer depends entirely upon the physical relations between  $S$ ,  $T$ ,  $F$ —that is to say, upon the kind of experiment we are making when we determine them. Every numerical law states both a mathematical relation and a physical relation; two laws in which the mathematical relation is the same may differ in their physical relations and *vice versa*. Thus the mathematical relations between the coordinates of a rectangular hyperbola referred to its asymptotes is the same as the mathematical relation between the pressure and volume of a perfect gas at constant temperature; but the physical relation is utterly different. Or, again, the physical relation of the coordinates of a hyperbola referred to its asymptotes is the same as the physical relation of the coordinates referred to any other axes, but the mathematical relation is different. Now it may happen that the physical relation between  $S$ ,  $T$ ,  $F$  is the same as that between  $s$ ,  $t$ ,  $f$  in (1)—that is to say,  $T$  may again be the period occupied by some particle in traversing a length  $S$ . In that case, and in that case only, (2) can be deduced by pure mathematical reasoning. For the statement that  $F$  is characteristic of the motion can only mean that in each system

$$S = \frac{1}{2} F T^2 \cdot \cdot \cdot \cdot \cdot \cdot (3);$$

if it does not mean that, the statement is not merely false,

but meaningless. (2) is a direct mathematical consequence of (3); it does not involve any additional assumption—such as that the systems are similar.

But when the question is raised, the physical relations of  $S$ ,  $T$ ,  $F$  are never actually those of (1); for example, the period of a pendulum is not the period occupied by a particle in falling down its length. When a difference of physical relationship is introduced, mathematics alone cannot possibly answer the question; for physical relations lie wholly outside the province of mathematics. In order to deduce from (1) anything about  $S$ ,  $T$ ,  $F$ , some assumption must be introduced concerning the physical connexion between these quantities and the  $s$ ,  $t$ ,  $f$  to which (1) refers. Such an assumption is the proposition that the systems are completely similar physically—that is to say that, if  $x_m$  is a magnitude of any kind characteristic of one system, then there is a magnitude of the same kind  $x_n$  characteristic of the other, and the ratio  $x_m/x_n$  is the same for all magnitudes of this kind. From this proposition the desired conclusion follows at once. For since the systems are characterised by accelerations, each of them must be characterised by a length and a period such that

$$s_m = \frac{1}{2} f_m t_m^2 \quad \text{and} \quad s_n = \frac{1}{2} f_n t_n^2. \quad \dots \quad (4)$$

$$\text{But} \quad \frac{S_m}{S_n} = \frac{s_m}{s_n}; \quad \frac{T_m}{T_n} = \frac{t_m}{t_n}; \quad \frac{F_m}{F_n} = \frac{f_m}{f_n}, \quad \dots \quad (5)$$

and (2) follows.

Here, again, the mathematical argument is so simple that it is hardly worth writing down; it certainly does not justify the introduction of the elaborate conception of invariance under transformation. The whole difficulty lies in the physical assumption of similarity. How are we to know that the systems are physically similar, unless we have such a complete knowledge of them that we are already aware of the proposition we profess to prove? The answer is, of course, that we never do know; we merely have reasons to suspect. The reasons may be of many different kinds; they may be good or bad; but they are always purely physical reasons, based, rightly or wrongly, on observations of the systems and not on jugglings with symbols. Thus, in the case of the pendulum, our reason is that the period of the pendulum seems to be the physical sum of elementary periods, during each of which it may be supposed to move with constant acceleration; that is a reason which can appeal only to those who have seen a

pendulum swing. In other cases, the reason may be much more complicated and far less immediately obvious ; but it is always a reason of the same kind.

If the logic of physical relations were developed as well as that of mathematical relations, it might be possible to reduce these reasons to some simple general principle. But it is not, and perhaps never will be. And while it is not, every application of the argument must be considered and judged individually. The matter is really even more difficult than has been suggested ; for very few, if any, systems are *completely* similar, and *complete* similarity is not actually required ; we have not to judge between the absence or presence of a definite quality, but of a degree of that quality sufficient for the immediate purpose. The only rule that can be given is, I think, that given in my previous paper \*. If we can write down a differential equation of the system, and if we know (this is a very large assumption) that the solution of it will lead to some relation involving the magnitudes between which we are seeking a law, then it is permissible to conclude that there is similarity between these magnitudes and those of the same kind involved in the differential equation.

These considerations are so simple and the conclusion, that it is impossible to express the argument in mathematical terms alone, is so obvious that some explanation seems to be needed why they have ever been overlooked. The cause is probably two-fold. First, it is thought that, if the argument attains without apparent mathematical argument results attainable otherwise only by the aid of complicated analysis, it must contain all that analysis somewhere in an exceedingly condensed form. But it does not attain the results of mathematical analysis ; it never proves anything in the mathematical sense, and it never leads to numerical values. Second, it is thought that what is common to all forms of the argument must be what is important in all forms. This is simply untrue. The important part of the argument, the proposition which leads to the valuable result or (if it is false) to error is different in different applications. If all the time and labour that have been devoted to elaborating irrelevant generalities had been devoted to a careful analysis of individual instances, it would have been a great deal better spent.

Finally, a few remarks may be offered on the examples of numerical laws from which Mrs. Ehrenfest-Afanassjewa

\* Phil. Mag. xlvii. p. 481 (1924).

starts her argument; for, although I am not quite sure what conclusion she draws from them, they illustrate well some complexities.

Law (ii.) involves a universal constant. The assignment of dimensions to such a constant expresses as usual the mathematical form of a numerical law. Accordingly, if we include the universal constant among the quantities characteristic of the system, we can make any deductions that could have been made if it had been a derived magnitude. But if we select the magnitudes characteristic of the system by noting how its behaviour changes when certain alterations are made, we shall be led to omit the universal constant and arrive at erroneous conclusions. The experimental fact that the period of geometrically similar pendulums changes only with changes in their length and gravitational acceleration does not establish (2); for there may be some law involving a numerical constant which has the same value for all pendulums whatever their length and whatever the gravitational acceleration. The neglect of this consideration is one of the most fruitful sources of error, which is deliberately encouraged by "dimensional analysis," but would certainly be avoided by Mrs. Ehrenfest-Afanassjewa's scheme.

In law (iii.),

$$f = ks/r, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where  $f$  is an angle,  $s$  the arc and  $r$  the radius, the dimensions of  $k$  give no indication of the form of the law and no conclusions can be drawn from them. But this apparent exception illustrates well the necessity for considering physical as well as mathematical relations.  $s$  and  $r$  are physically different; the experimenter has no difficulty in deciding whether he is measuring an arc or a radius. The experimental fact that  $f$  is proportional to the ratio  $s/r$  would emerge equally well if  $s$  and  $r$  were measured in different units; but it would not emerge if  $s$  or  $r$  were measured sometimes in one unit and sometimes in another. In fact, the same measuring instrument would not actually be used for  $s$  and  $r$ ; different instruments would be used and one calibrated in terms of the other. This calibration is a mere convenience in comparing our results with those of others. If we are to get the most out of the essentially physical argument from dimensions, we must neither include anything unessential to experiment nor exclude anything essential. Physically distinct magnitudes must be distinguished, and

the possibility of measuring them in different units recognised. If this is done,  $k$  has the dimensions (angle)  $\cdot$  (radius)  $\cdot$  (arc) $^{-1}$ , and the dimensions represent as usual the form of the law.

It may be pointed out that this example is exactly analogous to that of the Child-Langmuir equation discussed in my previous paper. There the failure of the argument arose from the confusion of the physically distinct lengths parallel and perpendicular to the field.

March 6th, 1926.

CIV. *Results of Crystal Analysis.* By L. VEGARD,  
Professor of Physics at the University of Oslo\*.

§ 1. **I**N previous papers† published in 1916 I gave the structure of the isomorphic minerals zircon ( $\text{ZrSiO}_4$ ), rutile ( $\text{TiO}_2$ ), and cassiterite ( $\text{SnO}_2$ ), and of the mineral anatase ( $\text{TiO}_2$ ). These structures were found by means of the ionization method of Bragg. Spectra of various orders for the  $\text{K}_\alpha$  line from Rh were obtained from the principal point-planes such as (100) (001) (110) (111).

At the same time I commenced with the same method the analysis of another interesting tetragonal group of which cheelite ( $\text{CaWO}_4$ ) and powellite ( $\text{CaMoO}_4$ ) are typical members. This analysis was not completed, and the results obtained were therefore not published.

Some years ago, when I had set up an arrangement for analysis by means of the powder method of Debye and Scherrer, I determined to apply this method to the analysis of these groups of minerals, partly to verify the results previously obtained by means of the spectrometer method and partly to complete the analysis of the cheelite group. This work was already completed two years ago, but as my time has been greatly absorbed by other investigations, the publication of the results was delayed.

The experimental arrangement has already been described in previous papers.

The reflexion angle ( $\phi$ ) of each line on the spectrogram

\* Communicated by the Author.

† L. Vegard: "Results of Crystal Analysis," *Phil. Mag.* xxxii. p. 65 (1916)—Paper I. *Ibid.*, III., *Phil. Mag.* xxxii. p. 505 (1916)—Paper II.



was found from the relation

$$\phi = \frac{l - \epsilon}{2r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $2l$  is the distance between two corresponding lines on the film (symmetrically situated with regard to the centre),  $r$  is radius of camera,  $\epsilon$  is a correction term characteristic of the camera and the substance, but which was found to be approximately independent of  $\phi$ .

The lines observed on the spectrogram are then to be identified or referred to corresponding point-planes of reflexion by means of the formula :

$$\left( \frac{2a}{\lambda} \sin \phi \right)^2 = \left( h_1^2 + h_2^2 + \left( \frac{a}{c} \right)^2 h_3^2 \right). \quad . \quad . \quad (2)$$

$a$  is the side of the basis,  $c$  the height of the elementary lattice,  $h_1, h_2, h_3$  the Millerian indices of the reflecting planes. A copper anticathode was used, and for the K-radiation we have

$$\lambda_\alpha = 1.54 \text{ \AA},$$

$$\lambda_\beta = 1.39 \text{ \AA}.$$

In the present case values of  $a$  and  $c$  were known from the previous observations by means of the ionization spectrometer.

The identification of the lines, therefore, merely required a direct calculation of both sides of the equation (2).

In order to obtain the best possible agreement between observed and calculated values throughout the whole spectrum, the dimensions of the elementary lattice ( $a$  and  $c$ ) had to be chosen slightly different from those found by the spectrometer method.

The main interest of this paper is attached to the exact determinations of the parameters of the lattices, which are based on considerations regarding the relative intensities of the lines. The observed relative intensities were directly estimated. This gives no accurate values, but we get the typical distribution of intensities, and that is sufficient for our present purpose.

The theoretical value of the intensities will be put proportional to the expression

$$I = \nu \left( \frac{S}{\sin \phi} \right)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $S$  is the structure factor,  $\nu$  the relative frequency of the reflecting planes.

I. ANATASE ( $\text{TiO}_2$ ).

§ 2. This crystal belongs to the ditetragonal, bipyramidal class, and the axis ratio  $\frac{c}{a} = 1.777$ .

My original analysis \* gave for the elementary lattice :

$$\begin{aligned} a &= 5.27 \text{ \AA}, \\ c &= 9.37 \text{ \AA}. \end{aligned}$$

The elementary lattice contains 8 molecules  $\text{TiO}_2$ .

The Ti-atoms were found to form a pseudocubic lattice of the diamond type.

The O-atoms were arranged in two lattices of the same type and placed in such a way that they can be brought to coincidence with the Ti-lattice through motions along a distance  $+l$  and  $-l$  respectively.

Thus the lattice has merely one parameter  $l$ , or we may more conveniently introduce an angular parameter

$$\gamma = 2\pi \frac{l}{c}.$$

By means of the spectrometer method I found

$$\frac{l}{c} = 5/24, \quad \text{or} \quad \gamma = 75^\circ.$$

Selecting a symmetry centre of the lattice as origin of the coordinates, we easily deduce the following simple equation for the structure factor S :

$$S = \cos A (\text{Ti} + 2\text{O} \cos h_3 \gamma), \quad . \quad . \quad . \quad (4)$$

where

$$A = \frac{\pi}{4} (h_1 + h_2 + h_3).$$

We have to consider the following three cases :

$$(a) \quad h_1 + h_2 + h_3 = 4n, \quad \text{then} \quad \cos A = \pm 1 \quad \text{and} \\ S = \text{Ti} + 2\text{O} \cos h_3 \gamma.$$

$$(b) \quad h_1 + h_2 + h_3 = 4n \pm 1, \quad \text{then} \quad \cos A = \pm \frac{1}{\sqrt{2}} \quad \text{and} \\ S = \frac{1}{\sqrt{2}} (\text{Ti} + 2\text{O} \cos h_3 \gamma).$$

$$(c) \quad h_1 + h_2 + h_3 = 4n + 2, \quad \text{then} \quad \cos A = 0 \quad \text{and} \\ S = 0.$$

\* Paper II.

Thus the lattice gives no reflexion for planes whose indices fulfil the condition  $\Sigma h = 2(2n + 1)$ , where  $n$  is a whole number.

The indices corresponding to the lines observed from anatase are given in Table I., and we see, in accordance with theory, that none of the observed lines fulfil the conditions (c).

From the intensities of the lines corresponding to case (a) we were able to conclude that the angle  $\gamma$  could not differ much from  $90^\circ$ , but for this group of lines we get the same intensity for  $90^\circ + \epsilon$  and  $90^\circ - \epsilon$ .

When, however, we take into account the second group (b) of lines, we find that  $\gamma$  must be smaller than  $90^\circ$ .

Then the intensities of the lines were calculated for a number of values of  $\gamma$  between  $70^\circ$  and  $80^\circ$ . The best correspondence between calculated and observed values was found for  $\gamma = 75^\circ$ , which is the very same value as that originally found, and thus the powder method gives exactly the same lattice as the Bragg reflexion method.

The results of our calculations both as regards position and intensities of the lines of the powder spectrum from anatase are given in Table I., and a graphical representation is given in fig. 1.

The space group of the lattice is  $D_{4h}^{19}$  after Niggli, which gives a symmetry of the crystal corresponding to the ditetragonal-bipyramidal class.

A model of the structure is given in my previous publication.

The positions of the atoms in a (110) plane are shown in fig. 2 A, and for a (100) plane are given in fig. 2 B.

The atoms belonging to the two face-centred lattices are marked I and II respectively.

From fig. 2 A we see that each O-atom is surrounded by three Ti-atoms. For the centre distances we get :

$$O_I - Ti = 1.99 \text{ \AA}$$

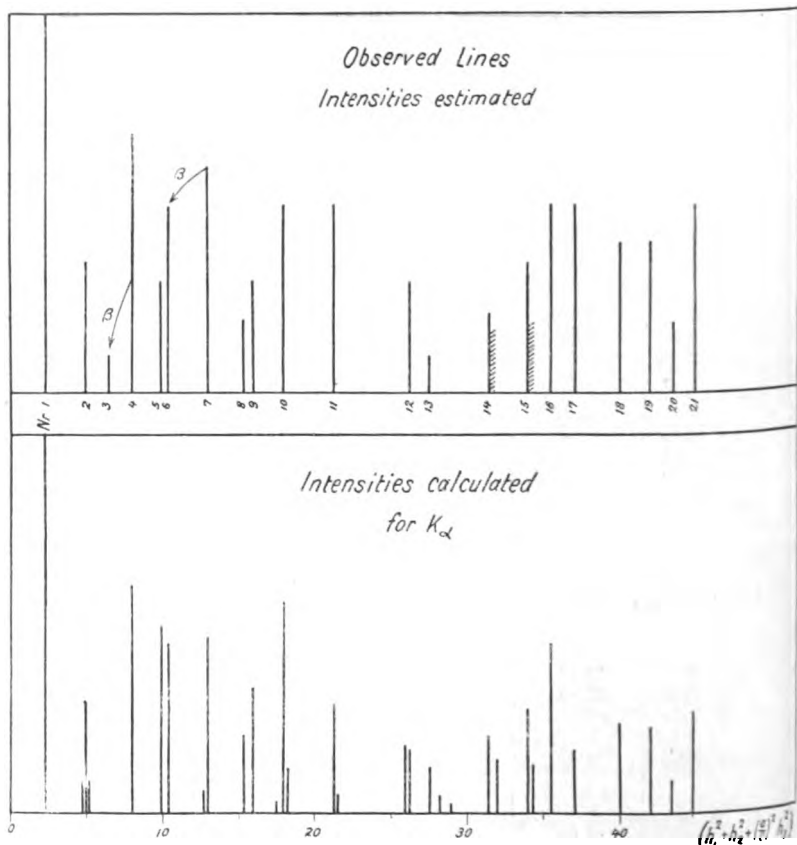
$$\text{and } O_{II} - Ti = \sqrt{\left(\frac{a}{4}\right)^2 - \left(\frac{1}{4} - l\right)^2 c^2} = 1.94 \text{ \AA}.$$

With the particular value of the parameter  $l$  derived from the X-ray analysis, we thus find that the two centre distances are very nearly equal. This means that we may regard the crystal as formed by packed spherical atoms.

TABLE I.  
Anatase,  $\text{TiO}_2$ .

$a = 5.37 \text{ \AA.} \quad c = 9.54 \text{ \AA.} \quad c/a = 1.777.$						
No.	$\phi^\circ$ .	$\left(\frac{2a}{\lambda} \sin \phi\right)^2$ .	$\left(h_1^2 + h_2^2 + \left(\frac{a}{c}\right)^2 h_3^2\right)$ .	$h_1 h_2 h_3$ .	I.	
					cal.	obs.
1	12.44	2.29	2.32	1.1.1	100	100
2	18.71	5.04	4.84	1.1.3	9	35
			5.06	0.0.4	30	
			5.26	2.0.2	9	
3	21.27	(7.88) <sub>B</sub>	(8.00)	(2.2.0)		
4	23.77	7.97	8.00	2.2.0	61	70
5	26.65	9.90	9.90	1.1.5	48	30
6	27.27	10.32	10.33	3.1.1	45	50
7	30.93	12.98	12.84	3.1.3	6	60
			13.06	2.2.4	47	
			15.37	2.0.6	21	
8	33.86	15.26	15.37	4.0.0	31	30
9	34.75	15.97	16.00	1.1.7	3	50
10	37.15	17.92	17.48	3.1.5	54	
			17.90	3.3.1	12	
			18.32	0.0.8	2	
11	41.02	21.16	20.22	3.3.3	2	50
			20.84	4.0.4	29	
			21.06	4.2.2	4	
12	46.87	26.13	25.48	3.1.7	1	30
			25.90	3.3.5	18	
			26.32	5.1.1	17	
13	48.64	27.41	27.60	1.1.9	13	10
14	53.24	31.55	28.22	2.2.8	5	20
			28.84	5.1.3	3	
			31.37	4.2.6	21	
15	56.64	34.28	32.00	4.4.0	15	35
			33.48	3.3.7	1	
			33.90	5.1.5	28	
16	58.68	35.87	34.32	5.3.1	13	50
			35.60	2.0.10	24	
			35.60	3.1.9	21	
17	60.77	37.42	36.84	5.3.3	2	40
			37.06	6.0.2	1	
			37.16	4.4.4	17	
18	64.84	40.27	40.00	6.2.0	24	40
19	67.87	42.18	40.24	1.1.11	3	
			40.48	5.1.7	1	
			41.90	5.3.5	23	40
20	71.16	43.60	43.60	3.3.9	9	20
21	74.30	45.11	45.06	6.2.4	27	50

Fig. 1.

Anatase  $\text{Ti O}_2$ 

If we put  $\gamma = 73^\circ.5$  instead of  $75^\circ$  the two centre distances would be the same and equal to  $1.95 \text{ \AA}$ , or indicating the atomic radius by  $\rho$ ,

$$\rho_0 + \rho_{\text{Ti}} = 1.95.$$

If now we assume oxygen to be present as a negative ion  $\text{O}^{--}$ , it should according to W. L. Bragg\* have a fairly large radius of about  $1.35 \text{ \AA}$ .

\* W. L. Bragg, Comm. from Roy. Inst. May 1, 1925.

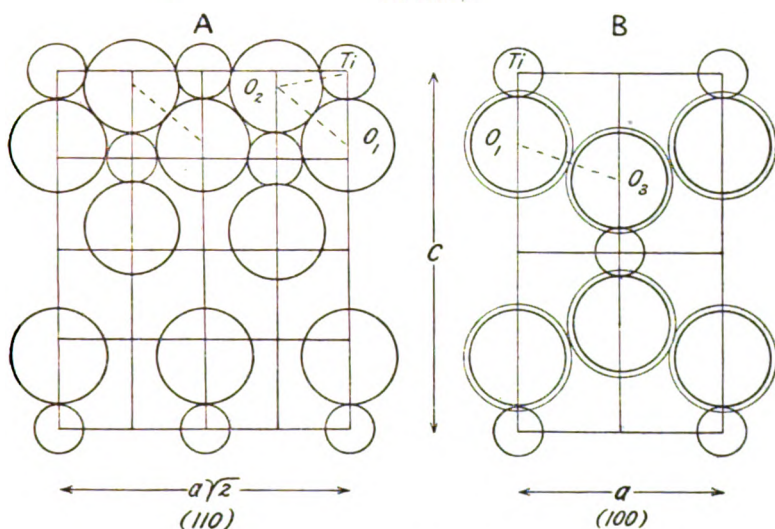
The question then arises whether the structure can allow for such large dimensions of the oxygen atoms.

For the centre distances between two oxygen atoms we get

$$O_1-O_2 = 2.48 \text{ \AA} \text{ (fig. 2 A),}$$

$$O_1-O_3 = \frac{2.79 \text{ \AA}}{\text{Mean}} \text{ (fig. 2 B).}$$

Fig. 2.  
*Anatase*



With the radius given by Bragg the centre distance in the case of contact would be 2.70, which is near to the mean value of the two centre distances found.

If the oxygen atoms are supposed to be a little deformed so as to be not perfectly spherical, we may assume that also the oxygen atoms are mutually in contact.

This means of course that this particular type of lattice gives a high degree of stability for the atoms Ti and O with their atomic dimensions. It is clear that with other diameters of the two atoms this lattice would no longer give the same stability. Perhaps this may explain why this type of lattice is not stable in the case of  $\text{SnO}_2$ .

Assuming the diameter of oxygen in  $\text{TiO}_2$  to be 2.64 Å, we get the radius of Ti :

$$\underline{\rho_{\text{Ti}} = 0.63 \text{ \AA}.}$$

## II. THE ZIRCON GROUP.

§ 3. In the paper published in 1916 the following structure was found for zircon:—

The elementary lattice ( $a=9.20 \text{ \AA}$ ,  $c=5.87 \text{ \AA}$ ) contained

TABLE II.—Zircon.

$a = 9.41 \text{ \AA}$ $c = 6.01 \text{ \AA}$ $c/a = 0.639$ .							
No.	$\phi^\circ$	$\left(\frac{2a}{\lambda} \sin \phi\right)^2$	$\left(h_1^2 + h_2^2 + \left(\frac{a}{c}\right)^2 h_3^2\right)$	$h_1 h_2 h_3$	$I_0$	$I_I$	$I_{II}$
1	13.59	8.25	4.45	1.1.1	70	25	35
			8.00	2.2.0		93	86
			12.45	3.1.1		26	4
2	17.77	13.95	13.80	2.0.2	50	68	58
3	19.23	16.21	16.00	4.0.0	10	12	10
4	20.33	18.03	17.80	2.2.2	5	19	7
5	21.79	20.58	20.45	3.3.1	30	13	28
6	23.67	24.06	24.05	1.1.3	30	5	21
7	24.77	(31.99) $_{\beta}$	(32.00)	(4.4.0)			
8	26.02	28.74	28.45	5.1.1	20	23	20
9	26.60	29.94	29.80	4.2.2	100	100	100
10	27.69	32.24	32.00	4.4.0	40	41	33
11	29.73	36.71	32.05	3.1.3			
			36.45	5.3.1		2	4
			39.20	0.0.4		21	9
12	31.25	40.18	40.00	6.2.0	35	40	28
			40.05	3.3.3			
			41.80	4.4.2		2	0
13	33.65	45.85	45.80	6.0.2	60	47	51
14	34.12	47.14	47.20	2.2.4	30	32	25
15	35.43	(61.72) $_{\beta}$	48.05	5.1.3		14	0
			49.80	6.2.2		5	1
			(61.80)	(6.4.2)			
16	36.67	52.26	52.45	5.5.1	15	10	17
17	37.46	55.23	52.45	7.1.1			
			55.20	4.0.4		7	21
18	38.77	(72.01) $_{\beta}$	56.05	5.3.3		1	6
			(72.00)	(6.6.0)			
			59.20	4.2.4		2	5
19	40.02	61.67	60.45	7.3.1		5	0
			61.80	6.4.2	25	30	19
			63.25	1.1.5		2	0
20	40.86	63.92	64.00	8.0.0	10	13	10
21	43.68	71.22	71.20	4.4.4	30	35	24
			71.25	3.1.5			
			72.00	6.6.0			
22	44.05	72.20	72.05	5.5.3	40	22	29
			72.05	7.1.3			
			76.45	7.5.1		11	3
23	46.14	77.63	77.80	8.2.2	50	28	29

TABLE II. (continued).—Zircon.

$a = 9.41 \text{ \AA.} \quad c = 6.01 \text{ \AA.} \quad c/a = 0.639.$							
No.	$\phi^\circ$ .	$\left(\frac{2a}{\lambda} \sin \phi\right)^2$ .	$\left(h_1^2 + h_2^2 + \left(\frac{a}{c}\right)^2 h_3^2\right)$ .	$h_1 h_2 h_3$ .	$I_0$ .	$I_L$ .	$I_{II}$ .
24	46.61	78.85	{ 79.20	{ 6.2.4	50	27	29
			{ 78.25	{ 3.3.5			
25	47.13	80.25	{ 80.00	{ 8.4.0	40	14	15
			{ 80.05	{ 7.3.3			
			{ 84.45	{ 9.1.1		1	0
			{ 87.25	{ 5.1.5		7	12
			{ 89.80	{ 8.4.2		0	2
			{ 91.20	{ 6.4.4		0	1
			{ 92.20	{ 2.0.6			
26	51.73	92.04	{ 92.45	{ 9.3.1	30	22	26
			{ 95.25	{ 5.3.5		1	2
			{ 96.05	{ 7.5.3			
27	53.19	95.71	{ 96.25	{ 2.2.6	10	13	10
			{ 100.45	{ 7.7.1		1	0
28	65.22	103.14	{ 103.20	{ 8.0.4	20	16	11
29	56.69	104.28	{ 104.00	{ 10.2.0	30	15	21
			{ 104.05	{ 9.1.3			
			{ 107.20	{ 8.2.4		1	4
			{ 108.20	{ 4.2.6			
30	58.26	107.99	{ 108.45	{ 9.5.1	25	33	20
			{ 109.80	{ 10.0.2			
31	59.15	110.06	{ 109.80	{ 8.6.2	50	26	28
			{ 111.20	{ 6.6.4			
32	59.46	110.75	{ 111.25	{ 5.5.5	20	24	17
			{ 111.25	{ 7.1.5			
			{ 112.05	{ 9.3.3		10	0
			{ 113.80	{ 10.2.2		1	1
			{ 119.20	{ 8.4.4			
33	63.33	119.25	{ 119.25	{ 7.3.5	50	16	22
			{ 120.05	{ 7.7.3			
			{ 120.20	{ 4.4.6		2	0
			{ 122.05	{ 1.1.7		1	0
			{ 124.20	{ 6.0.6			
			{ 124.45	{ 11.1.1		24	9
34	66.83	126.20	{ 125.80	{ 10.4.2	60	24	28

8 molecules  $\text{ZrSiO}_4$ . The Zr- as well as the Si-atoms were arranged in pseudocubic lattices of the diamond type displaced relative to each other a distance  $c/2$  along the tetragonal axis.



The 32 oxygen atoms inside each elementary lattice were divided in two equal groups, one of which was considered to be closely attached to the Zr- and the second to the Si-atoms.

The oxygen atoms were not arranged in pseudocubic lattices of the diamond type, but in face-centred lattices.

The lines obtained by means of the powder method are given in Table II.

The first column gives the No. of the lines in the order of increasing reflexion angle  $\phi$ . The second column contains the values of  $\phi$ .

It appeared that the structure already found gave the right interpretation of all the lines observed.

The third column gives for each line the values of

$$\left(\frac{2a \sin \phi}{\lambda}\right)^2,$$

and the fourth one the corresponding values of

$$h_1^2 + h_2^2 + \left(\frac{a}{c}\right)^2 h_3^2,$$

from which we find the Millerian indices of the reflecting planes (see equation 2). These indices are given in the fifth column.

The column headed  $I_0$  contains relative intensities of the lines as they are estimated from the film.

A few faint lines on the spectrogram are due to a reflexion of  $K_\beta$ , and these lines are in the table indicated by  $\beta$ .

As already mentioned, the structure found may be regarded as composed of face-centred lattices, and, taking a point midway between two neighbouring Zr-atoms as the origin of our coordinate system, the basis group of face-centred lattices is given by the following coordinates:—

The Zr-atoms:

$$\left[\frac{1}{8}, \frac{1}{8}, \frac{1}{8}\right] \quad \text{and} \quad \left[-\frac{1}{8}, -\frac{1}{8}, -\frac{1}{8}\right].$$

The Si-atoms:

$$\left[\frac{1}{8}, \frac{1}{8}, \frac{5}{8}\right] \quad \text{,,} \quad \left[-\frac{1}{8}, -\frac{1}{8}, +\frac{3}{8}\right].$$

The O-atoms:

$$\left. \begin{aligned} &\left[\frac{1}{8} + \epsilon_1, \frac{1}{8} + \epsilon_1, \frac{1}{8}\right], \quad \left[\frac{1}{8} - \epsilon_1, \frac{1}{8} - \epsilon_1, \frac{1}{8}\right] \\ &\left[-\frac{1}{8} + \epsilon_1, -\frac{1}{8} - \epsilon_1, -\frac{1}{8}\right], \quad \left[-\frac{1}{8} - \epsilon_1, -\frac{1}{8} + \epsilon_1, -\frac{1}{8}\right] \end{aligned} \right\} \text{connected to Zr.}$$

$$\left. \begin{aligned} &\left[\frac{1}{8} + \epsilon_2, \frac{1}{8} + \epsilon_2, \frac{5}{8}\right], \quad \left[\frac{1}{8} - \epsilon_2, \frac{1}{8} - \epsilon_2, \frac{5}{8}\right] \\ &\left[-\frac{1}{8} + \epsilon_2, -\frac{1}{8} - \epsilon_2, \frac{5}{8}\right], \quad \left[-\frac{1}{8} - \epsilon_2, -\frac{1}{8} + \epsilon_2, \frac{5}{8}\right] \end{aligned} \right\} \text{connected to Si.}$$

To obtain the whole basis group of simple lattices we have merely to remember that to each coordinate ( $x y z$ ) correspond three other points with the coordinates :

$$(x + \frac{1}{2}, y + \frac{1}{2}, z), \quad (x + \frac{1}{2}, y, z + \frac{1}{2}), \quad \text{and} \quad (x, y + \frac{1}{2}, z + \frac{1}{2}).$$

Introducing the coordinates of the basis group into the general formula for the structure factor, we get after some reduction :

$$\begin{aligned} S = F [ & \cos A \{ \text{Zr} + (-1)^{h_2} \text{Si} + \text{O} (\cos (h_1 - h_2) \alpha_1 + \cos (h_1 + h_2) \alpha_1 \\ & + (-1)^{h_2} \cos (h_1 - h_2) \alpha_2 + \cos (h_1 + h_2) \alpha_2) \} \\ & - i \text{O} \sin A \{ \cos (h_1 - h_2) \alpha_1 - \cos (h_1 + h_2) \alpha_1 \\ & + (-1)^{h_2} \cos (h_1 - h_2) \alpha_2 - (-1)^{h_2} \cos (h_1 + h_2) \alpha_2 \} ], \end{aligned}$$

. . . (5)

where

$$A = \frac{\pi}{4} (h_1 + h_2 + h_3),$$

$$\alpha_1 = 2\pi e_1,$$

$$\alpha_2 = 2\pi e_2.$$

The chemical symbols stand for the atomic numbers.

The common factor  $F$  is the structure factor characteristic of the face-centred lattice :

$$F = [1 + (-1)^{h_2+h_3} + (-1)^{h_1+h_3} + (-1)^{h_1+h_2}].$$

Thus, if the indices ( $h_1 h_2 h_3$ ) are partly even and partly odd,  $F \equiv 0$  and the intensity of the corresponding line is zero.

As a matter of fact we see from Table II. that no line with mixed indices is observed, consequently the crystal of zircon is composed of *face-centred lattices*.

When the indices are either all even or all odd,  $F = 4$ .

We may therefore equally well drop the factor  $F$  and the equation (5) can be given the following simpler form :

$$\begin{aligned} S = & \cos A [ \text{Zr} + (-1)^{h_2} \text{Si} + 2\text{O} (\cos h_1 \alpha_1 \cos h_2 \alpha_1 \\ & + (-1)^{h_2} \cos h_1 \alpha_2 \cos h_2 \alpha_2) ] \\ & - i 2\text{O} \sin A (\sin h_1 \alpha_1 \sin h_2 \alpha_1 + (-1)^{h_2} \sin h_1 \alpha_2 \sin h_2 \alpha_2). \end{aligned}$$

. . . (6)

We may distinguish between the following three cases :—

(a)  $h_1 + h_2 + h_3 = 4n$  ; then  $\cos A = \pm 1$ ,  $\sin A = 0$ ,

$$S = Zr + Si + 2O(\cos h_1\alpha_1 \cos h_2\alpha_1 + \cos h_1\alpha_2 \cos h_2\alpha_2).$$

(b)  $h_1 + h_2 + h_3 = 4n \pm 1$  ; then  $\cos A = \pm \frac{1}{\sqrt{2}}$ ,  $\sin A = \pm \frac{1}{\sqrt{2}}$ .

$$S = \frac{1}{\sqrt{2}} [Zr - Si + 2O(\cos h_1\alpha_1 \cos h_2\alpha_1 - \cos h_1\alpha_2 \cos h_2\alpha_2) \\ \times i2O \operatorname{tg} A(\sin h_1\alpha_1 \sin h_2\alpha_1 - \sin h_1\alpha_2 \sin h_2\alpha_2)].$$

(c)  $h_1 + h_2 + h_3 = 4n + 2$  ; then  $\cos A = 0$ ,  $\sin A = \pm 1$ .

$$S = 2O(\sin h_1\alpha_1 \sin h_2\alpha_1 + \sin h_1\alpha_2 \sin h_2\alpha_2).$$

The lines corresponding to case (c) are entirely due to the oxygen atoms, and the existence of lines of this group would show that the oxygen atoms cannot be arranged in lattices of the diamond type like Zr and Si. This is *e. g.* shown by the existence of a line with the indices (222) which was also found in my first investigations by means of the ionization method.

In the case of the lines of class (a) the wavelets from the Zr- and Si-atoms are in phase, while in the case of group (b) there is a phase difference of  $\pi$ , so the amplitudes are subtracted. The phase difference between waves from Zr- and Si-atoms depends on the actual displacement of the two lattices. The rule above mentioned is obtained from a displacement  $c/2$  along the  $c$ -axis.

Now we find that all lines of group (a) are strong as compared with those of group (b), and this shows that we are right in assuming a mutual displacement of  $c/2$ .

If we introduce the parameters previously found,

$$\alpha_1 = 75^\circ, \quad \alpha_2 = 30^\circ,$$

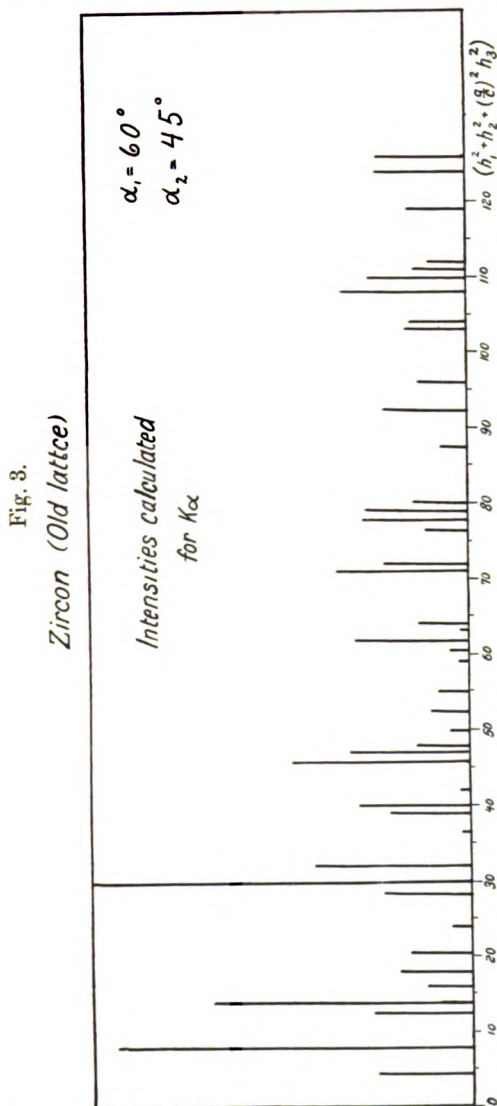
we obtain an intensity distribution which has essential features in common with that observed, but there are some differences which indicate that the positions of the oxygen atoms are not quite correctly determined.

We have then tried to improve the agreement by taking other values of the parameters, and we obtain perhaps a somewhat better intensity distribution by putting

$$\alpha_1 = 60^\circ \quad \text{and} \quad \alpha_2 = 45^\circ.$$

The intensities calculated on this assumption are indicated by  $I_1$  and given in Table II. and in fig. 3.

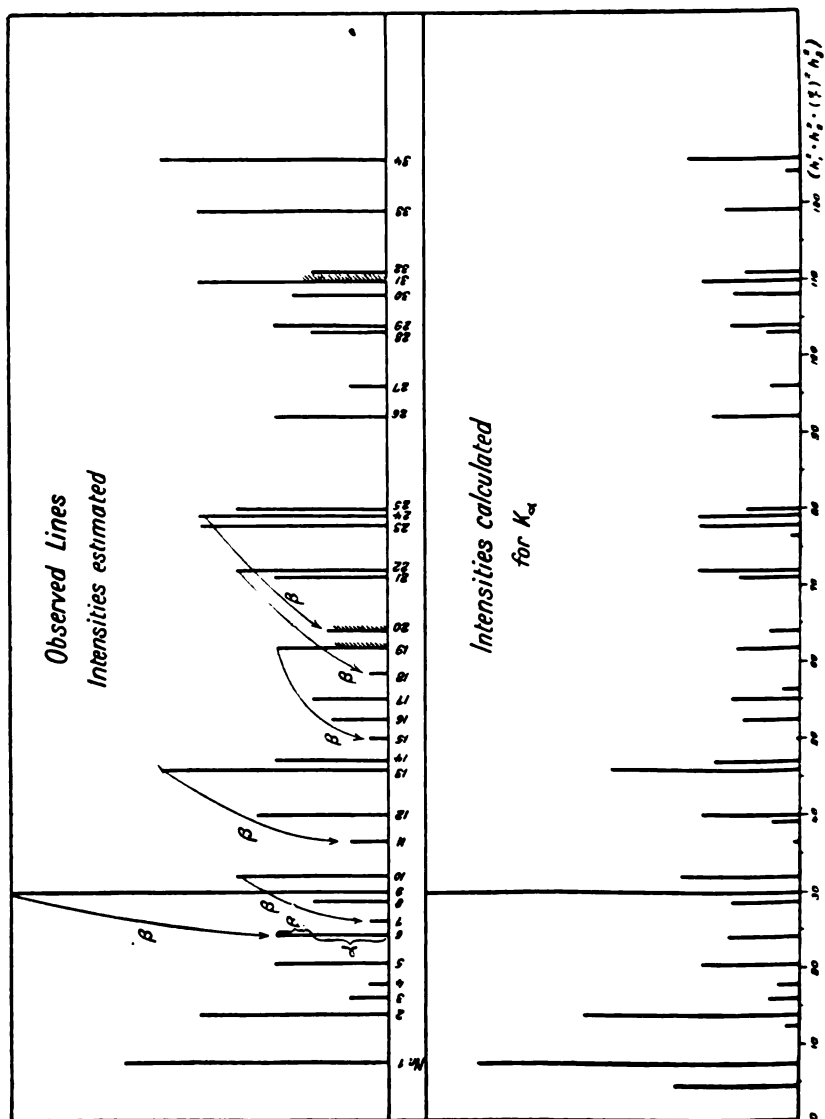
Comparing these intensities with those observed  $I_0$  (fig. 4 and Table II.), we notice that the calculated and observed intensities differ in a quite marked way for the lines No. 3,



4, 5, 6 corresponding to (400), (222), (331), and (113). We may say that the calculated intensities of No. 3, 5, 6 come out too weak as compared with that of No. 4.

Further, the calculations give a too large intensity for the (311) line, which is too weak to be observed.

Fig. 4.  
Zircon,  $\text{ZrSiO}_4$



It seems therefore necessary in some way to introduce new parameters for the oxygen atoms.

Before proceeding further, we shall make a few remarks

regarding the symmetry of our lattices as compared with that found for the crystal.

According to P. Groth, 'Chemische Kristallographie,' zircon belongs to the ditetragonal-bipyramidal class.

Now the space lattice given for the Zr- and Si-atoms would give this symmetry, but when the arrangement proposed for the oxygen atoms is taken into account, there is no longer any reflecting plane perpendicular to the  $c$ -axis. The lattice corresponds to a ditetragonal-pyramidal crystal symmetry.

The space lattice belongs to the space group  $C_{4v}^{11}$ . This space group, however, has more parameters than introduced in our lattice. The space group  $C_{4v}^{11}$  is characterized by :

- (1) Pseudo-diamond lattices movable along the  $c$ -axis.
- (2) Point groups corresponding to the coordinate of the oxygen atoms and movable along the  $c$ -axis.

This point group gives in fact three new parameters, which do not disturb the symmetry, one parameter determining the displacement of the Si-atoms, and two parameters for the displacement of each of the two oxygen groups.

Now we saw, however, that the mutual displacement of Zr and Si is  $c/2$ , and this suggests that there probably may be found such positions for the oxygen atoms that the lattice will have a reflexion plane perpendicular to  $c$ .

If we call the displacement of the two oxygen groups  $\eta_1 c$  and  $\eta_2 c$ , the arrangement of the oxygen atoms takes the form of a single group with bipyramidal symmetry, if we put

$$\epsilon_1 + \epsilon_2 = \frac{1}{4} \quad \text{and} \quad \eta_1 + \eta_2 = \frac{1}{4}.$$

If these conditions are fulfilled, we get only two parameters :

$$\epsilon = \epsilon_1 \quad \text{and} \quad \eta = \eta_1,$$

because we have

$$\epsilon = \frac{1}{4} - \epsilon \quad \text{and} \quad \eta_2 = \frac{1}{4} - \eta.$$

At the same time we pass over into the space group  $D_{4h}^{19}$  of higher symmetry. This is the same space group as found for anatase.

The construction points of the 8 face-centred lattices of the oxygen atoms have the coordinates :

$$\begin{aligned} & \left[ \left[ \frac{1}{8} + \epsilon, \frac{1}{8} + \epsilon, \frac{1}{8} + \eta \right], \left[ \frac{1}{8} - \epsilon, \frac{1}{8} - \epsilon, \frac{1}{8} + \eta \right], \right. \\ & \left. \left[ \frac{1}{8} - \epsilon, \frac{1}{8} + \epsilon, \frac{1}{8} - \eta \right], \left[ \frac{1}{8} + \epsilon, \frac{1}{8} - \epsilon, \frac{1}{8} - \eta \right], \right. \\ & \left[ -\frac{1}{8} - \epsilon, -\frac{1}{8} - \epsilon, -\frac{1}{8} - \eta \right], \left[ -\frac{1}{8} + \epsilon, -\frac{1}{8} + \epsilon, -\frac{1}{8} - \eta \right], \\ & \left. \left[ -\frac{1}{8} + \epsilon, -\frac{1}{8} - \epsilon, -\frac{1}{8} + \eta \right], \left[ -\frac{1}{8} - \epsilon, -\frac{1}{8} + \epsilon, -\frac{1}{8} + \eta \right] \right]. \end{aligned}$$

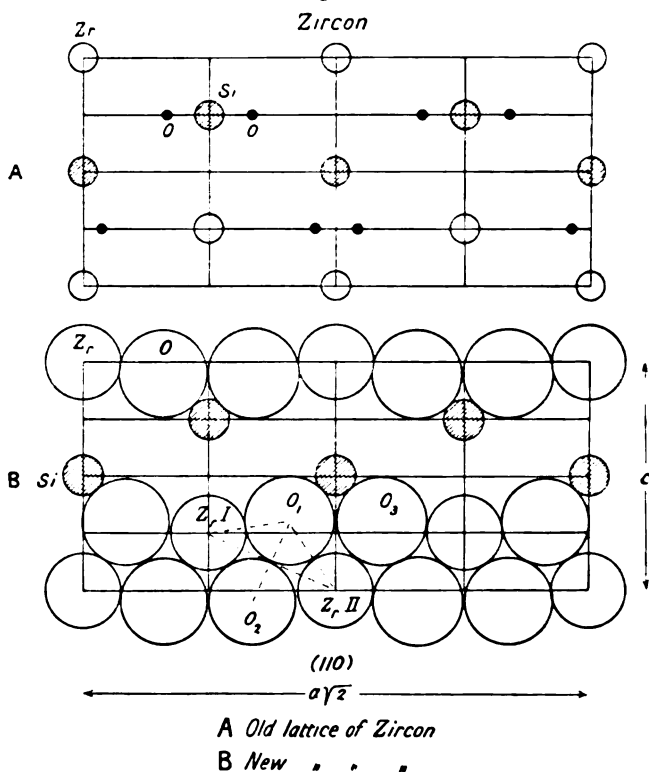
For the structure factor we deduce the formula :

$$S = \cos A (Zr + (-1)^k Si + 4O \cos h_1 \alpha \cos h_2 \alpha \cos h_3 \gamma) \\ + 4O \sin A \sin h_1 \alpha \sin h_2 \alpha \sin h_3 \gamma. \quad (7)$$

We can now as before consider the cases (a), (b), (c) corresponding to

$$\Sigma h = 4n, \quad \Sigma h = 4n \pm 1, \quad \text{and} \quad \Sigma h = 4n + 2.$$

Fig. 5.



If in this formula we put

$$\alpha = 56^\circ \quad \text{and} \quad \gamma = 20^\circ,$$

and calculate the intensities by means of (7) and (3), we get the intensities  $I_{II}$  given in the last column of Table II.

Comparing the calculated and observed values, we notice

that the calculated intensities give the right type of variation throughout the whole spectrum\*.

A point of great interest is that the relative intensities of the lines 3, 4, 5, 6 are now correct. The agreement between theory and observations is even better seen from fig. 4, where the calculated intensities are given underneath the observed ones.

In addition to the good representation of the intensities also comes that the modified lattice gives the right symmetry of the crystal, and I think there can be no doubt that we have found the right structure of zircon.

In this model all oxygen atoms are equal. Each atom of Zr or Si is surrounded by a group of four oxygen atoms, which are nearly placed at the corners of a tetrahedron. The structure corresponds to the formula  $\text{ZrSiO}_4$ .

The new position of the oxygen atoms is well illustrated if we consider the atoms in a (110) plane. The old and the new arrangements are shown in fig. 5.

### *Dimensions of the Atoms.*

§ 4. We notice that each oxygen atom is situated near two Zr-atoms and one Si-atom. A simple calculation gives for the centre distances :

$$\rho_{\text{O}} + \rho_{\text{Zr(I)}} = 2.10 \text{ \AA.}$$

$$\rho_{\text{O}} + \rho_{\text{Zr(II)}} = 2.22 \text{ ,,}$$

$$\rho_{\text{O}} + \rho_{\text{Si}} = 1.72 \text{ ,,}$$

We see that the distances from the O-atom to the two Zr-atoms are very nearly equal. If we may regard the atoms as spheres in contact, the true value of the parameters ought to make the two centre distances equal.

As in the case of anatase we assume oxygen to exist in the form of negative ions  $\text{O}^{--}$ , with large diameters, and we are then led to consider the possibility that also the oxygen ions are in contact with each other. We shall have to consider distances between atoms like  $\text{O}_1-\text{O}_2$  or  $\text{O}_1-\text{O}_3$  (fig. 5 B),

\* It should be remarked that the first of the calculated lines (111) is not found on the spectrogram on account of blackening of the film. The first order reflexion from (111), however, was found by means of the ionization method to be stronger than the following orders, and this is in agreement with the calculated intensities as seen from Table II.



and we find :

$$\text{Distance } O_1-O_2 = 2.34 \text{ \AA.}$$

$$,, \quad O_1-O_3 = 2.43 ,,$$

These distances are also approximately equal and of proper magnitude.

If now we regard the atoms as spheres in contact, the two parameters would be fixed without ambiguity by the two conditions of contact :

$$\text{Distance } Zr_{(1)}-O_1 = Zr_{(11)}-O_1,$$

$$,, \quad O_1-O_2 = O_1-O_3.$$

From these conditions we deduce the following equations :

$$\left. \begin{aligned} \epsilon - \frac{1}{2} \left( \frac{c}{a} \right)^2 \eta &= \frac{1}{16} \left\{ 2 + \left( \frac{c}{a} \right)^2 \right\}, \\ \epsilon + \frac{1}{2} \left( \frac{c}{a} \right)^2 (\eta + 4\eta^2) &= \frac{1}{16} \left\{ 3 - \frac{1}{2} \left( \frac{c}{a} \right)^2 \right\}, \end{aligned} \right\} \quad . \quad . \quad (8)$$

which give

$$\epsilon = 0.161, \quad \alpha = 58^\circ.0,$$

$$\eta = 0.0535, \quad \gamma = 19^\circ.3.$$

These parameters give :

$$\text{Minimum centre distance } O-O = 2.36 \text{ \AA.}$$

$$,, \quad ,, \quad ,, \quad Zr-O = 2.17 ,,$$

$$,, \quad ,, \quad ,, \quad Si-O = 1.67 ,,$$

and for the ionic dimensions :

$$\rho_O = 1.18 \text{ \AA.}$$

$$\rho_{Zr} = 0.99 ,,$$

$$\rho_{Si} = 0.49 ,,$$

The radius here found for the oxygen atoms is very nearly the same as the radius found in the case of anatase. The contact conditions in the (110) plane gave in that case  $\rho_O = 1.24 \text{ \AA.}$

The structure of zircon regarded as formed by spheres of the dimensions here given is a most compact one. This will be seen from fig. 5 B. The apparent gap is filled by atoms having their centres outside the plane of the drawing.

### III. RUTILE AND CASSITERITE. $\text{TiO}_2$ and $\text{SnO}_2$ .

§ 5. Like zircon, the crystals of rutile and cassiterite belong to the ditetragonal-bipyramidal class.

The ratios  $c/a$  are for zircon 0.6391, for rutile 0.6439, and for cassiterite 0.6726. The three minerals were therefore regarded as isomorphous.

In my previous investigations I found that the lattice of rutile and cassiterite could be obtained from the zircon lattice by specifying the values of the parameters. As, however, Zr and Si were replaced by equal atoms, this substitution increased the symmetry in the way that the lattice of rutile and cassiterite got reflexion planes perpendicular to the  $c$ -axis. To put it short, through the substitution the lattice passed over from the space group  $C_{4v}^{11}$  to the group  $D_{4h}^{14}$ .

Now we found, however, that the zircon lattice had to be slightly modified with regard to the position of the oxygen atoms. By a proper choice of oxygen parameters we were able to raise the symmetry from that of the space group  $C_{4v}^{11}$  to that of  $D_{4h}^{19}$ , and in this way we obtained the right zircon structure.

It is now a question of considerable importance to know whether the lattices of rutile and cassiterite can be derived by specifying the parameters of the zircon lattice, or whether they have the structure which was found in my first investigations. In the latter case zircon will not be exactly isomorphous with the two other minerals.

The lines of the spectra and the usual data concerning intensities and identifications of lines are given in Tables III. and IV. for rutile and cassiterite respectively.

We shall first consider the lattice which was previously found by means of the ionization method.

The structure factor is found from (5) by putting  $a_1 = a_2 = a$  and substituting Zr and Si with Ti resp. Sn. Then we get

$$S = (1 + (-1)^k) [\cos A \{M + 2O \cos h_1 \alpha \cos h_2 \alpha\} + i 2O \sin A \sin h_1 \alpha \sin h_2 \alpha], \quad (9)$$

where  $M$  is the atomic number of the metal Ti or Sn.

TABLE III.—Rutile,  $\text{Ti}_2\text{O}_4$ .

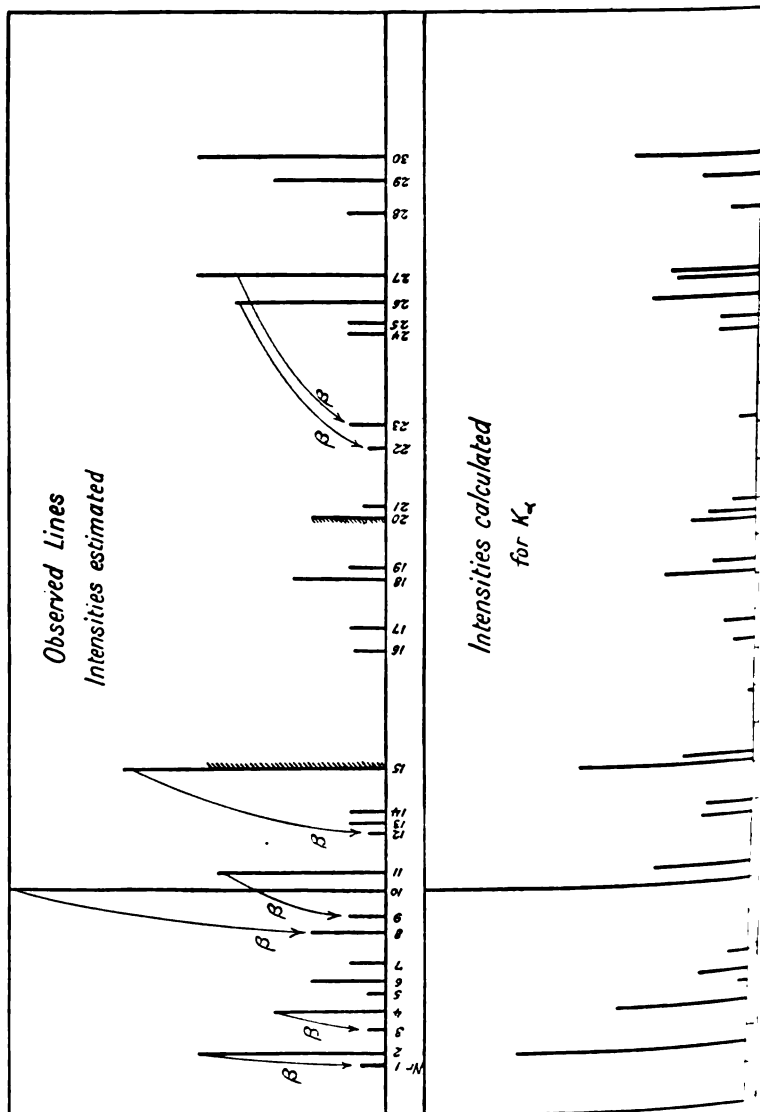
$a = 9.30 \text{ \AA.}$ $c = 5.98 \text{ \AA.}$ $c/a = 0.643.$						
No.	$\phi^\circ$ .	$\left(\frac{2a}{\lambda} \sin \phi\right)^2$ .	$\left(h_1^2 + h_2^2 + \left(\frac{a}{c}\right)^2 h_3^2\right)$ .	$h_1 h_2 h_3$ .	I.	
					cal.	obs.
1	12.28	(8.05) $_{\beta}$	(8.00)	(2.2.0)		
2	13.53	8.00	8.00	2.2.0	76	50
3	16.15	(13.76) $_{\beta}$	(13.64)	(2.0.2)		
4	17.87	13.74	13.64	2.0.2	47	30
5	19.33	16.01	16.00	4.0.0	5	5
6	20.38	17.70	17.64	2.2.2	30	20
7	21.79	20.12	20.00	4.2.1	9	10
8	23.88	(29.18) $_{\beta}$	(29.64)	(4.2.2)		
9	24.98	(31.77)	(32.00)	(4.4.0)		
10	26.80	29.68) $_{\beta}$	29.64	4.2.2	100	100
11	27.85	31.88	32.00	4.4.4	36	40
12	30.41	(45.64) $_{\beta}$	(45.64)	(6.0.2)		
13	33.93	38.58	38.58	0.0.4	20	10
14	31.56	40.00	40.00	6.2.0	18	10
15	34.01	45.67	41.64	4.4.2	0	
			45.64	6.0.2	59	
					} 70	
			46.58	2.2.4	26	
			49.64	6.2.2	0	
			52.00	6.4.0	0	
			54.58	4.0.4	3	
			58.58	4.2.4	0	
16	40.60	61.84	61.64	6.4.2	9	10
17	41.43	63.92	64.00	8.0.0	12	10
18	44.10	70.71	68.00	8.2.0	0	
			70.58	4.4.4	33	25
19	44.83	72.57	72.00	6.6.0	16	10
20	47.18	78.54	77.64	8.2.2	24	
			78.58	6.4.2	18	20
21	47.91	80.40	80.00	8.4.0	9	5
22	50.98	(106.91) $_{\beta}$	81.64	6.6.2	0	
			(106.80)	(4.2.6)		
			89.64	8.4.2	0	
23	52.15	90.95	90.80	2.0.6	7	10
			90.58	6.4.4	0	
			94.80	2.2.6	0	
			102.58	8.0.4	15	10
24	56.90	102.45	104.00	10.2.0	15	10
25	57.53	103.94	106.80	4.2.6	28	40
26	59.15	107.62	106.58	8.2.4	0	
			109.64	8.6.2		
					28	
27	60.56	110.73	109.64	10.0.2		
			110.58	6.6.4	32	50
			113.64	10.2.2	0	
			116.00	10.4.0	0	
28	64.89	119.66	118.58	8.4.4	12	10
			118.80	4.4.6	0	
			122.80	6.0.6	22	30
29	66.98	123.68	125.64	10.4.2	43	50
30	68.80	126.92				

TABLE IV.—Cassiterite,  $\text{Sn}_2\text{O}_4$ .

$a = 9.45 \text{ \AA.} \quad c = 6.36 \text{ \AA.} \quad c/a = 0.673.$						
No.	$\phi^\circ$	$\left(\frac{2a}{\lambda} \sin \phi\right)^2$	$\left(h_1^2 + h_2^2 + \left(\frac{a}{c}\right)^2 h_3^2\right)$	$h_1 h_2 h_3$	I.	
					cal.	obs.
1	13.43	8.13	8.00	2.2.0	82	60
2	15.41	(13.09) $_{\beta}$	(12.84)	(2.0.2)		
3	17.09	13.02	12.84	2.0.2	82	80
4	19.07	16.09	16.00	4.0.0	22	20
			16.84	2.2.2	7	
			20.00	4.2.0	2	
5	23.30	(29.00) $_{\beta}$	(28.84)	(4.2.2)		
6	24.61	(32.15) $_{\beta}$	(32.00)	(4.4.0)		
7	26.02	29.00	28.84	4.2.2	100	100
8	27.54	32.33	32.00	4.4.0	28	30
9	29.00	35.43	35.36	0.0.4	15	15
10	29.52	(44.99) $_{\beta}$	(44.84)	(6.0.2)		
11	31.04	40.08	40.00	6.2.0	27	30
			40.84	4.4.2	0	
12	32.50	43.52	43.63	2.2.4	31	30
13	33.13	45.03	44.84	6.0.2	44	40
			48.84	6.2.2	2	
14	35.84	51.68	51.36	4.0.4	14	20
			52.00	6.4.0	0	
			55.36	4.2.4	2	
15	39.50	60.99	60.84	4.6.2	27	35
16	40.65	63.97	64.00	8.0.0	12	15
17	42.01	67.50	67.36	4.4.4	27	30
			68.00	8.2.0	2	
18	43.68	71.89	72.00	6.6.0	13	15
19	44.94	75.22	75.36	6.2.4	28	35
20	45.61	77.00	76.84	8.2.2	32	40
21	46.76	80.00	80.00	8.4.0	14	20
			80.84	6.6.2	0	
22	48.28	83.95	83.56	2.0.6	12	15
			87.36	6.4.4	0	
			87.56	2.2.6	1	
			88.84	8.4.2	1	
23	50.11	(109.18) $_{\beta}$	(108.84)	(8.6.2)		
24	52.20	(115.77) $_{\beta}$	(115.36)	(8.4.4)		
			99.56	4.2.6		
25	54.34	99.50	99.36	8.0.4	44	50
			103.36	8.2.4	2	
26	56.12	103.90	104.00	10.2.0	15	15
27	57.58	107.41	107.36	6.6.4	17	20
			108.84	10.0.2		
28	58.21	108.88	108.84	8.6.2	31	40
			111.56	4.4.6	0	
			112.84	10.2.2	0	
			115.56	6.0.6		
29	61.03	115.37	115.36	8.4.4	35	50
			119.56	6.2.6	1	
30	65.31	124.41	124.84	10.4.2	35	50
31	66.93	127.60	128.00	8.8.0	5	15
32	69.02	131.42	131.56	6.4.6	12	40
			135.36	8.6.4	0	
33	71.34	135.44	136.03	10.6.0	5	20
			136.84	8.8.2	1	
34	73.72	138.90	139.36	10.2.4	21	50

Remembering that all reflexions from faces with mixed indices vanish, we see that faces with odd indices give no

Fig. 6.

Rutile  $\text{Ti}_2\text{O}_4$ 

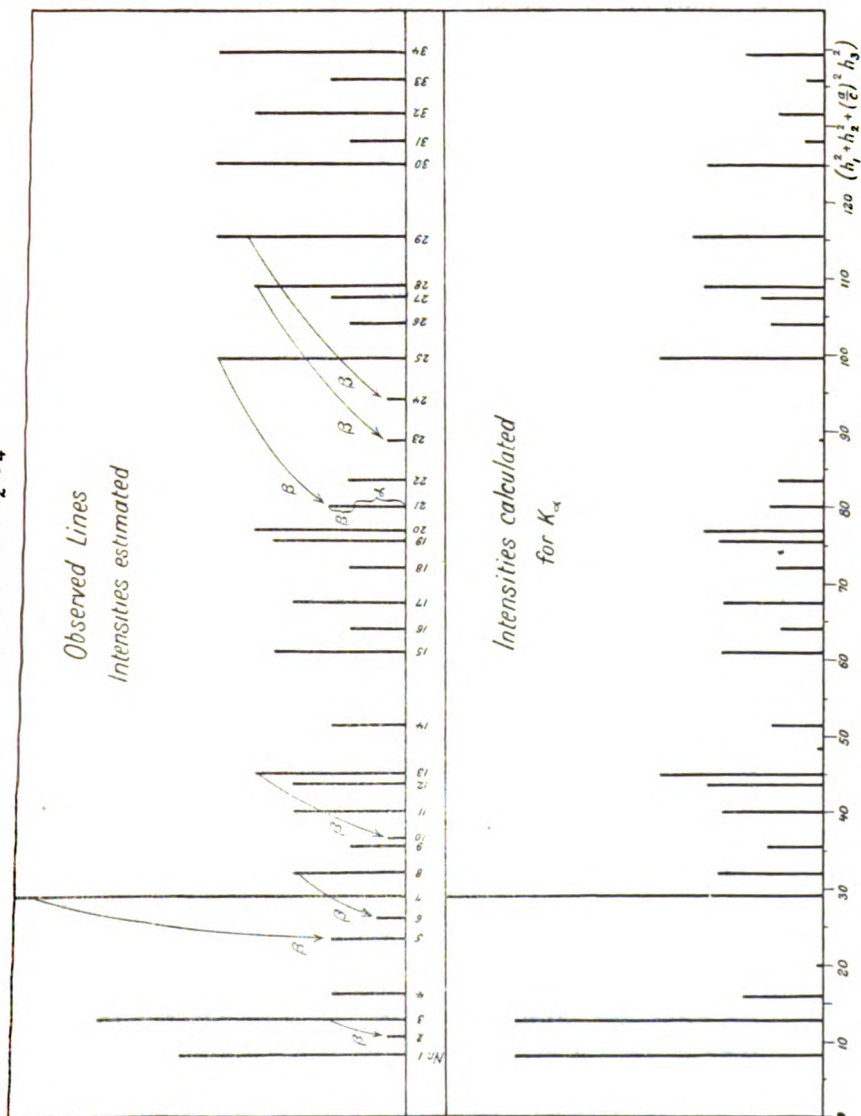
reflexion, because  $(1 + (-1)^{h+k}) = 0$ . We may also say that faces for which  $\Sigma h = 4n \pm 1$  give no reflexion.

This is also in accordance with observations. We have

therefore only to consider the two cases :

- (1)  $\Sigma h = 4n$ ,  $S = M + 2O \cos h_1 \alpha \cos h_2 \alpha$  ;
- (2)  $\Sigma h = 4n + 2$ ,  $S = 2O \sin h_1 \alpha \sin h_2 \alpha$ .

Cassiterite  $\text{Sn}_2\text{O}_4$



As the lines of the second group result only from the O atoms, these lines must as a rule be weak as compared with those of the first group.

As a matter of fact, we find that the lines of the first group dominate the spectrum.

In the case of  $\text{SnO}_2$  the reflexion from Sn is so dominating that only lines of the first group appear. Rutile, however, shows the lines (222) and (420) corresponding to case (2).

The parameters originally found were:

For rutile,  $\alpha = 55^\circ 75$ .

For cassiterite,  $\alpha = 56^\circ 25$ .

We have here calculated the intensities by putting  $\alpha = 54^\circ$  for both minerals.

The intensities calculated in this way are given in the Tables III. and IV. and graphically represented in figs. 6 and 7. The agreement between the observed and calculated intensity distribution is seen to be remarkably good.

If on the other hand we would apply the zircon lattice, we come into conflict with observed facts.

The structure factor derived from that of zircon takes the form:

$$(1) \quad \Sigma h = 4n, \quad S = \text{Ti} + 2\text{O} \cos h_1\alpha \cos h_2\alpha \cos h_3\gamma,$$

$$(2) \quad \Sigma h = 4n + 2, \quad S = 2\text{O} \sin h_1\alpha \sin h_2\alpha \sin h_3\gamma,$$

$$(3) \quad \Sigma h = 4n \pm 1, \quad S = \frac{1}{\sqrt{2}} 2\text{O} \left\{ \begin{array}{l} \cos h_1\alpha \cos h_2\alpha \cos h_3\gamma \\ + \sin h_1\alpha \sin h_2\alpha \sin h_3\gamma \end{array} \right\}.$$

In this case lines of odd indices should appear, but no line of this group is observed. It might be argued, however, that these lines were merely too faint to show up on the film. It is therefore also of special importance to consider the lines (222) and (420). They are both observed, but according to the above formula (case 2) the line (420) should vanish because  $\sin h_3\gamma = 0$ .

On account of the space filling conditions  $\gamma$  must be very small, and the above formula would therefore give an intensity for the (222) line which is too small to explain its appearance on the film.

We therefore conclude that the structure originally found for rutile and cassiterite is right, and these minerals with a space group  $D_{4h}^{14}$  are not exactly isomorphous with zircon with a space group  $D_{4h}^{19}$ .

The considerable difference between the structure of zircon and that of rutile and cassiterite will be seen by

comparing fig. 5 and fig. 8, giving the atomic arrangements in the (110) planes for these minerals. The difference is also

Fig. 8.

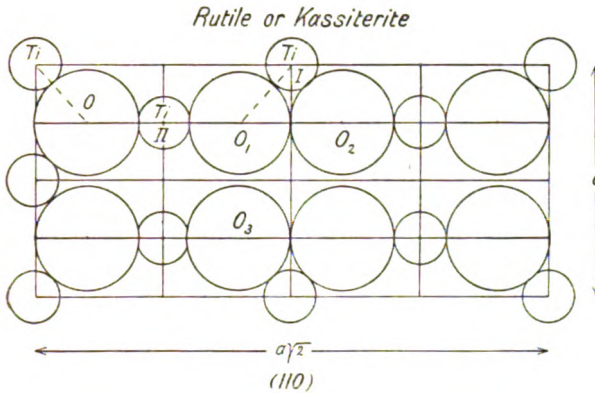
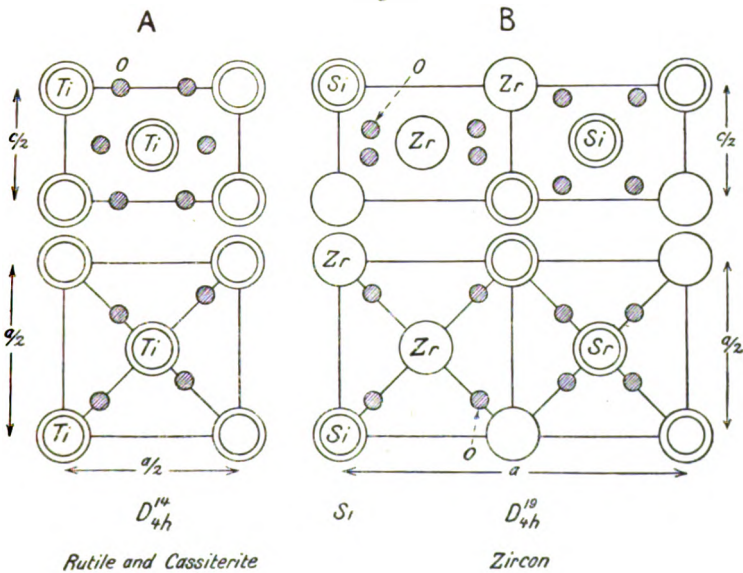


Fig. 9.



clearly seen by comparing fig. 9 A and fig. 9 B, giving the horizontal and vertical projection of the two lattices.



*Dimensions of the Atoms.*

§ 6. From fig. 8 we easily deduce the distance from the O-centres to those of the nearest Ti- resp. Sn-atoms.

For rutile,

$$\rho_{\text{O}} + \rho_{\text{Ti}}(\text{I}) = 1.97 \text{ \AA.}$$

$$\rho_{\text{O}} + \rho_{\text{Ti}}(\text{II}) = 1.99 \text{ ,,}$$

For cassiterite,

$$\rho_{\text{O}} + \rho_{\text{Sn}}(\text{I}) = 2.00 \text{ \AA.}$$

$$\rho_{\text{O}} + \rho_{\text{Sn}}(\text{II}) = 2.08 \text{ ,,}$$

The two centre distances are very nearly equal. We can, as before, find such parameters as will make them exactly equal.

From these conditions we get for the parameters :

For rutile,

$$\epsilon = 0.151, \quad \alpha = 54^{\circ}.3.$$

For cassiterite,

$$\epsilon = 0.153, \quad \alpha = 55^{\circ}.2.$$

Applying these parameter values, the minimum centre distance for two oxygen atoms like  $\text{O}_1$  and  $\text{O}_2$ , fig. 8, will be :

$$\text{For rutile, } \text{O}_1 - \text{O}_2 = 2.62 \text{ \AA.}$$

$$\text{For cassiterite, } \text{,,} = 2.60 \text{ ,,}$$

If we consider these oxygen atoms to be spheres in contact, we can find the following dimensions for the spherical ions :

$$\text{Rutile, } \rho_{\text{O}} = 1.31 \text{ \AA.}, \quad \rho_{\text{Ti}} = 0.67 \text{ \AA.}$$

$$\text{Cassiterite, } \rho_{\text{O}} = 1.30 \text{ ,,}, \quad \rho_{\text{Sn}} = 0.75 \text{ ,,}$$

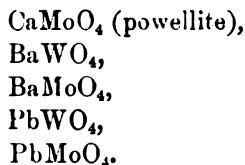
TABLE V.

Substance.	Space group.	Dimensions of elementary lattice.		Parameters.		Radius of ions.	
		a.	c.	$\epsilon$ .	$\eta$ .	Negative (oxygen).	Positive.
Anatase .....	$\text{D}_{4h}^{19}$	5.37 $\overset{\circ}{\text{\AA}}$ .	9.54 $\overset{\circ}{\text{\AA}}$ .	.....	0.204	1.32 $\overset{\circ}{\text{\AA}}$ .	Ti 0.63 $\overset{\circ}{\text{\AA}}$ .
Rutile .....	$\text{D}_{4h}^{14}$	9.30 ..	5.98 ..	0.151	.....	1.31 ..	Ti 0.67 ..
Cassiterite ...	..	9.45 ..	6.36 ..	0.153	.....	1.30 ..	Sn 0.75 ..
Zircon .....	$\text{D}_{4h}^{19}$	9.41 ..	6.01 ..	0.161	0.0535	1.18 ..	Zr 0.99 .. Si 0.49 ..

For the sake of comparison the constants of the lattices of the minerals anatase, zircon, rutile, and cassiterite are collected in Table V.

#### IV. THE STRUCTURE OF THE SCHEELITE GROUP.

§ 7. The crystals of the mineral Scheelite belong to the tetragonal-bipyramidal class. Isomorphous with scheelite we have a number of other minerals like



With regard to chemical formula, these minerals bear some resemblance to zircon  $\text{ZrSiO}_4$ , but the crystal form differs both as regards symmetry, class, and axis ratio  $c/a$ , which in the case of the scheelite group is about  $3/2$ , while for zircon  $c/a$  was only  $0.64$ .

An analysis of the scheelite group was commenced in 1916 by means of the ionization method, and for scheelite itself the following results were obtained :

The elementary lattice contained 8 molecules  $\text{CaWO}_4$ . The side of the base was found to be  $a = 7.48 \text{ \AA}$ . and the height  $c = 11.3 \text{ \AA}$ . It was further found that both the Ca- and W-atoms were arranged in pseudo-cubic lattices of the diamond type displaced relative to each other a distance  $c/2$  in the direction of the  $c$ -axis.

Any definite result regarding the arrangement of the oxygen atoms was not obtained at that time. The expansion of the lattice in the  $c$ -direction would suggest that the oxygen atoms were similarly arranged as for anatase, in such a way that Ca and W formed centres of a group O-W-O with its axis in the  $c$ -direction. This arrangement, however, gave no satisfactory agreement with observations.

In order to determine accurately the positions of the oxygen atom, spectrograms after the method of Debye-Scherrer were taken, to begin with only for the minerals scheelite and powellite ; but later on the investigations were extended to other members of the group.

The knowledge already gained by means of the Bragg method was sufficient for the interpretation of the lines on the spectrogram.

In Tables VI. and VII. are given the observed lines. The first column contains the current number of the lines in the

order of increasing reflexion-angle  $\phi$ , given in the second column.

TABLE VI.—Scheelite,  $\text{CaWO}_4$ .

$a=7.44 \text{ \AA.}$ $c=11.35 \text{ \AA.}$ $c/a=1.537.$ $\alpha=20^\circ.$ $\beta=20^\circ.$ $\gamma=72^\circ.$						
No.	$\phi^\circ.$	$\left(\frac{2a}{\lambda} \sin \phi\right)^2$	$\left(h_1^2+h_2^2+\left(\frac{a}{c}\right)^2 h_3^2\right)$	$h_1 h_2 h_3.$	I.	
					cal.	obs.
1	12.91	$(5.72)_\beta$	2.43 (5.72) 5.72	1.11 (2.0.2) 2.0.2	28	
2	14.37	5.75	5.86	1.13	100	100
3	15.52	6.68	6.86	0.04	26	10
4	17.09	8.06	8.00	2.2.0	40	35
5	19.44	10.33	10.43	3.1.1	19	25
6	21.26	$(15.08)_\beta$	$(14.86)$ 12.73	$(2.2.4)$ 1.1.5	2	
7	22.52	13.68	13.86	3.1.3	16	10
8	23.56	14.80	14.86	2.2.4	39	50
9	24.56	16.11	16.00	4.0.0	18	30
10	25.94	$(21.80)_\beta$	$(21.72)$ 18.43	$(4.2.2)$ 3.3.1	6	
11	27.22	19.29	19.44	2.0.6	33	35
12	28.00	20.57	20.73 21.72	3.1.5 4.2.2	8	10
13	28.95	21.84	21.86 22.86	3.3.3 4.0.4	66	60
14	29.68	22.86	23.02	1.1.7	33	30
15	32.29	26.60	26.43 27.46	5.1.1 0.0.8	9 4	15
16	33.75	28.79	28.73	3.3.5	5	15
17	34.49	29.91	29.86	5.1.3	6	10
18	35.22	31.02	31.02	3.1.7	7	10
19	35.95	32.15	32.00 34.43 35.44	4.4.0 3.5.1 4.2.6	4 7	10
20	38.40	35.41	35.46 36.73	2.2.8 5.1.5	44	55
			36.75 37.72	1.1.9 6.0.2	8	
21	39.55	37.81	37.86 38.86	5.3.3 4.4.4	22	25
22	40.25	38.93	39.02	3.3.7	13	15
23	41.17	40.42	40.00	6.2.0	13	15
24	43.21	43.40	43.46 44.73	4.0.8 5.3.5	13	20
25	43.94	44.93	44.75	3.1.9	13	10

TABLE VI. (continued).

No.	$\phi^\circ$ .	$\left(\frac{2a}{\lambda} \sin \phi\right)^2$	$\left(h_1^2 + h_2^2 + \left(\frac{a}{c}\right)^2 h_3^2\right)$	$h_1 h_2 h_3$	I.	
					cal.	obs.
26	45.20	46.95	46.86	6.2.4	44	50
			46.90	2.0.10		
			47.02	5.1.7		
			50.43	5.5.1		
27	47.88	51.29	50.43	7.1.1	12	15
			51.44	6.0.6		
			52.75	3.3.9		
			53.72	6.4.2		
			53.86	5.5.3		
28	49.48	53.89	53.86	7.1.3	33	40
			53.91	1.1.11		
			55.02	5.3.7		
			58.43	7.3.1		
29	52.77	59.14	59.46	4.4.8	15	10
			60.73	7.1.5		
30	53.92	60.03	60.73	5.5.5	10	15
			60.75	5.1.9		
			61.78	0.0.12		
			61.86	7.3.3		
31	55.18	62.87	61.91	3.1.11	14	20
			62.90	4.2.10		
32	56.22	63.96	64.00	8.0.0	8	5
			67.44	6.2.8		
33	58.31	67.54	67.46	6.4.6	33	50
			68.73	7.3.5		
			68.75	5.3.9		
			69.78	2.2.12		
34	59.88	69.77	69.72	8.2.2	21	30
			69.91	3.3.11		
			70.86	8.0.4		
35	60.98	71.32	71.02	5.5.7	13	25
			71.02	7.1.7		
			72.00	6.6.0		
36			74.43	7.5.1	3	10
			77.78	4.0.12		
37	65.68	77.44	77.86	7.5.3	12	25
			77.91	5.1.11		
			78.86	6.6.4		
38	66.83	78.83	78.90	6.0.10	17	30
			79.02	7.3.7		
39	67.85	80.10	80.00	8.4.0	7	10
			82.43	9.1.1		
40	70.90	83.92	83.44	8.2.6	12	30
			84.75	5.5.9		
			84.75	7.1.9		
			84.73	7.5.5		
41	75.03	87.07	85.86	9.1.3	7	40
			85.91	5.3.11		
			86.86	8.4.4		

TABLE VII.—Powellite,  $\text{CaMoO}_4$ .

$a = 7.40 \text{ \AA.}$ $c = 11.44 \text{ \AA.}$ $c/a = 1.546.$ $\alpha = 20^\circ.$ $\beta = 20^\circ.$ $\gamma = 72^\circ.$						
No.	$\phi^\circ.$	$\left(\frac{2a}{\lambda} \sin \phi\right)^2$	$\left(h_1^2 + h_2^2 + \left(\frac{c}{a}\right)^2 h_3^2\right)$	$h_1 h_2 h_3$	I.	
					cal.	obs.
1	13.17	(5.90) $\beta$	2.42 (5.67)	1.1.1 (2.0.2)	7	
2	14.32	5.65	5.67	2.0.2	100	100
3	15.62	6.70	5.77	1.1.3	37	10
4	17.19	8.08	6.70	0.0.4	52	30
5	19.44	10.24	8.00	2.2.0	15	15
6	21.00	(14.60) $\beta$	10.42 (14.70)	3.1.1 (2.2.4)		
			12.47	1.1.5	0	
7	23.51	14.70	13.77	3.1.3	11	
8	24.56	15.97	14.70	2.2.4	51	60
9	25.86	(21.63) $\beta$	16.00 (21.67)	4.0.0 (4.2.2)	23	30
10	26.96	19.01	18.42 19.07	3.3.1 2.0.6	45	40
			20.47	3.1.5	3	
11	29.00	21.73	21.67	4.2.2	88	70
			21.77	3.3.3		
12	29.68	22.67	22.70	4.0.4	39	20
13	32.39	26.62	22.51 26.42	1.1.7 5.1.1	8	10
			26.80	0.0.8	2	
14	33.70	28.45	28.47	3.3.5	5	10
			29.77	5.1.3	4	
15	34.95	30.18	30.51	3.1.7	5	10
16	36.52	32.74	32.00	4.4.0	3	10
			34.42	3.5.1		
17	37.93	34.94	34.80	2.2.8	59	90
			35.07	4.2.6		
			35.91	1.1.9	0	
			36.47	5.1.5	3	
			37.67	6.0.2		
18	39.71	37.74	37.77 38.51	5.3.3 3.3.7	23	30
			38.70	4.4.4	13	
19	41.12	39.99	40.00	6.2.0	15	20
20	42.74	42.58	42.80	4.0.8	16	10
			43.91	3.1.9	3	
			44.47	5.3.5	8	
			45.86	2.0.10	26	
21	45.09	46.38	46.51	1.5.7	24	60
			46.70	6.2.4		

TABLE VII. (continued).

No.	$\phi^\circ$ .	$\left(\frac{2a}{\lambda} \sin \phi\right)^2$ .	$\left(h_1^2 + h_2^2 + \left(\frac{c}{a}\right)^2 h_3^2\right)$ .	$h_1 h_2 h_3$ .	I.	
					cal.	obs.
			50.42	5.5.1		
			50.42	7.1.1	3	
22	47.91	50.91	51.07	6.0.6	15	30
			51.91	3.3.9	1	
			52.65	1.1.11	0	
23	49.64	53.67	53.67	6.4.2		
			53.77	5.5.3	38	50
			53.77	7.1.3		
			54.51	5.3.7	0	
24	52.67	58.48	58.42	7.3.1	2	
			58.80	4.4.8	23	10
			59.91	5.1.9		
			59.98	0.0.12	5	
25	53.82	60.25	60.47	5.5.5		10
			60.47	7.1.5	4	
26	54.86	61.83	61.86	4.2.10	15	30
27	56.12	63.71	64.00	8.0.0	12	5
			66.80	6.2.8		
28	58.15	66.70	67.07	6.4.6	41	80
			67.91	5.3.9		
			67.98	2.2.12	11	
			68.47	7.3.5	3	
			68.65	3.3.11	0	
29	60.24	69.66	69.67	8.2.2	13	
			70.51	5.5.7		50
			70.51	7.1.7	16	
			70.70	8.0.4		
			72.00	6.6.0	3	
			74.42	7.5.1	2	
			75.98	4.0.12		
30	65.10	76.06	76.65	5.1.11	12	20
			77.77	7.5.3		
31	66.77	78.07	77.86	6.0.10	12	20
			78.51	7.3.7		
			78.70	6.6.4	8	
32	68.45	80.00	80.00	8.4.0	8	20
			82.42	9.1.1		
33	71.16	82.81	83.07	8.2.6	15	60
			83.91	5.5.9		
			83.91	7.1.9	2	
			84.47	7.5.5		
			84.65	5.3.11	5	
			85.77	9.1.3	4	
34	75.08	86.32	86.70	8.4.4	17	30

The correctness of the identification of lines is seen from columns 3 and 4. The fifth column gives the indices of the lines, and the last two columns give observed and calculated intensities.

At the head of each table are given the dimensions of the lattice and the values of the parameters used for calculating the intensities. We shall see later on that these parameters must probably be slightly modified to suit the space-filling conditions of the atoms.

### *Symmetry of the Lattice.*

§ 8. The arrangement of the metal atoms was found by the Bragg method, and this result was confirmed by the Debye-Scherrer spectrograms. If we look at the structure apart from the oxygen atoms, the lattice of Ca and W in scheelite has exactly the same symmetry as that of Zr and Si in zircon—both belong to the space group  $D_{4h}^{19}$ .

In the case of zircon also the oxygen atoms were arranged in accordance with this space group. Scheelite, however, has the lower symmetry of the tetragonal-bipyramidal class, and if this degradation of symmetry is not due to an asymmetry of the centres, we are led to suppose that the oxygen atoms are arranged in a space group which has no reflexion plane parallel to the (110) plane.

The symmetry elements parallel to the  $c$ -axis, which are characteristic of the lattice of Ca-W (space group  $D_{4h}^{19}$ ) are illustrated in fig. 10. There is one system of right screw axis, one of left screw axis, and one system of diagonal axis.

Parallel to (110) are reflexion planes (drawn in full) and gliding reflexion planes (dotted lines). Parallel to (100) are gliding reflexion planes (dotted).

The arrangement of Ca- and W-atoms around one of the screw axes is shown in fig. 11.

In addition, the lattice has gliding reflexion planes perpendicular to the  $c$ -axis. The planes  $(001)_{1/8}$  and  $(001)_{3/8}$  with gliding components  $\frac{a_x}{4} + \frac{a_y}{4}$  and the planes  $(001)_{5/8}$  and  $(001)_{7/8}$  with gliding components  $\frac{a_x}{4} - \frac{a_y}{4}$ .

When we take into account the oxygen atoms, the lattice loses the symmetry planes parallel to the  $c$ -axis, but we assume the tetragonal screw axis and the horizontal reflexion planes to be preserved. The lattice then corresponds to the space group  $C_{4h}^6$ .

The lattice containing 8 molecules must contain 32 oxygen atoms.

Fig. 10.

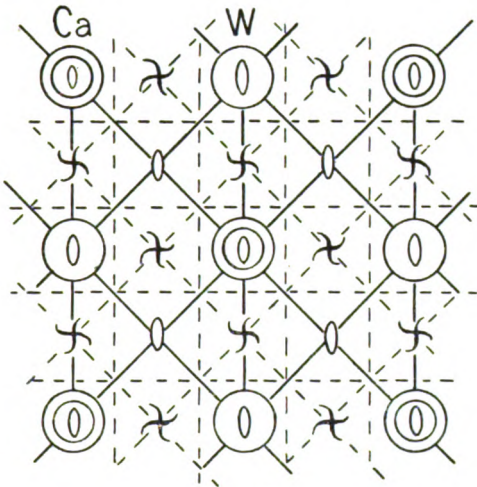
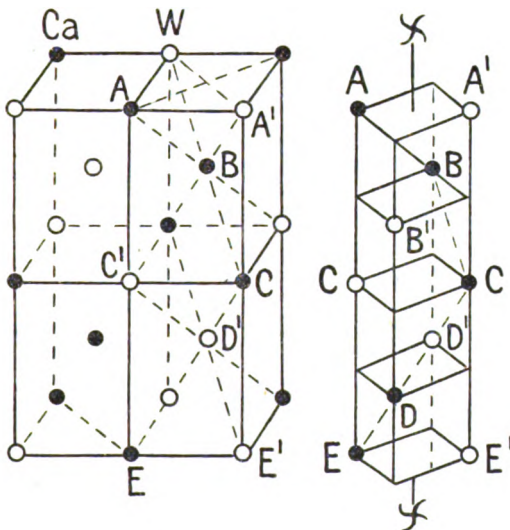


Fig. 11.



The space group gives two groups of eight points without degrees of freedom. These positions are occupied by the Ca- and W-atoms. The space group gives further two



groups of sixteen points without degrees of freedom and one group of sixteen with one degree of freedom. An arbitrary point with three parameters has 32 equivalent positions. If, therefore, the oxygen atoms are to be arranged according to  $C_{4h}^6$ , we must either divide them in two groups of 16 or in one group of 32 with three parameters. Only the last arrangement can explain the symmetry of the crystal.

*Structure Factor and Intensities.*

§ 9. We place the coordinate system with the axis parallel to  $a$  and  $c$  and with the origin at the centre of one of the Ca-atoms. Let the coordinates of one O-atom be :

$$\begin{aligned}x &= la, \\y &= ma, \\z &= nc.\end{aligned}$$

The coordinates of the other 31 atoms are then found by applying the symmetry conditions of the lattice. We then find that the oxygen atoms may be regarded as arranged in 8 face-centred lattices.

Taking the symmetry centre  $(\frac{1}{8} \frac{1}{8} \frac{1}{8})$  as origin of the coordinate system, the positions of the 8 face-centred lattices are given by the coordinates :

$$\begin{aligned}&[\frac{1}{8}+l, \frac{1}{8}+m, \frac{1}{8}+n], \quad [\frac{1}{8}-l, \frac{1}{8}-m, \frac{1}{8}+n], \\&[\frac{1}{8}+m, \frac{1}{8}-l, \frac{1}{8}-n], \quad [\frac{1}{8}-m, \frac{1}{8}+l, \frac{1}{8}-n], \\&[-\frac{1}{8}-l, -\frac{1}{8}-m, -\frac{1}{8}-n], \quad [-\frac{1}{8}+l, -\frac{1}{8}+m, -\frac{1}{8}-n], \\&[-\frac{1}{8}-m, -\frac{1}{8}+l, -\frac{1}{8}+n], \quad [-\frac{1}{8}+m, -\frac{1}{8}-l, -\frac{1}{8}+n].\end{aligned}$$

The structure factor of the oxygen atoms :

$$\begin{aligned}\frac{S}{O} &= 2F \left[ \cos 2\pi \left( \frac{\Sigma h}{8} + h_1 l + h_2 m + h_3 n \right) \right. \\&\quad + \cos 2\pi \left( \frac{\Sigma h}{8} - h_1 l - h_2 m + h_3 n \right) \\&\quad + \cos 2\pi \left( \frac{\Sigma h}{8} + h_1 m - h_2 l - h_3 n \right) \\&\quad \left. + \cos 2\pi \left( \frac{\Sigma h}{8} - h_1 m + h_2 l - h_3 n \right) \right], \quad \dots \quad (10)\end{aligned}$$

where

$$F = 1 + (-1)^{h_2+h_3} + (-1)^{h_1+h_3} + (-1)^{h_1+h_2}$$

is the structure factor of the face-centred lattice, which

is =0 for mixed indices. When the indices are either all even or all odd,  $F=4$ . This consequence is so far in agreement with observations, because no line corresponding to mixed indices appears on the spectrogram.

We put

$$\begin{aligned}\frac{\pi}{4}(h_1 + h_2 + h_3) &= A, \\ 2\pi l &= \alpha + \beta, \quad \alpha = 2\pi \frac{l+m}{2}, \\ 2\pi m &= \alpha - \beta, \quad \beta = 2\pi \frac{l-m}{2}, \\ 2\pi n &= \gamma.\end{aligned}$$

Excluding the cases of mixed indices for which  $S = 0$ , we get :

$$\begin{aligned}\frac{S}{8O} &= \cos [A + h_1(\alpha + \beta) + h_2(\alpha - \beta) + h_3\gamma] \\ &+ \cos [A - h_1(\alpha + \beta) - h_2(\alpha - \beta) + h_3\gamma] \\ &+ \cos [A + h_1(\alpha - \beta) - h_2(\alpha + \beta) - h_3\gamma] \\ &+ \cos [A - h_1(\alpha - \beta) + h_2(\alpha + \beta) - h_3\gamma] \\ &= 2\{ \cos (A + h_3\gamma) \cos [h_1(\alpha + \beta) + h_2(\alpha - \beta)] \\ &+ \cos (A - h_3\gamma) \cos [h_1(\alpha - \beta) - h_2(\alpha + \beta)] \},\end{aligned}$$

which after some reduction gives :

$$\begin{aligned}\frac{S}{32O} &= \cos A \cos (h_1\alpha - h_2\beta) \cos (h_2\alpha + h_1\beta) \cos h_3\gamma \\ &+ \sin A \sin (h_1\alpha - h_2\beta) \sin (h_2\alpha + h_1\beta) \sin h_3\gamma.\end{aligned}$$

If in this formula we put  $\alpha = \beta = \gamma = 0$ , the points assume the position of the Ca-atoms. Remembering that 4 points join in each Ca-centre, we obtain for the structure factor of Ca :

$$\frac{S}{8 \cdot \text{Ca}} = \cos A.$$

Putting  $\alpha = \beta = 0$  and  $\gamma = \pi$ , we obtain the structure factor of the W atoms :

$$\frac{S}{8W} = (-1)^{h_3} \cos A.$$

Dividing by  $32O$ , we finally obtain for the structure factor of the whole lattice :

$$\begin{aligned}\frac{S}{\cos A} &= \frac{\text{Ca} + (-1)^{h_3}W}{4O} + \cos (h_1\alpha - h_2\beta) \cos (h_2\alpha + h_1\beta) \cos h_3\gamma \\ &+ \text{tg } A \cdot \sin (h_1\alpha - h_2\beta) \sin (h_2\alpha + h_1\beta) \sin h_3\gamma\end{aligned}\quad (11)$$

Putting  $Ca=20$ ,  $W=74$ ,  $O=8$ , we obtain :

$$(1) \Sigma h=4n, \cos A=\pm 1, \sin A=0.$$

$$S = 2.938 + \cos(h_1\alpha - h_2\beta) \cos(h_2\alpha + h_1\beta) \cos h_3\gamma.$$

$$(2) \Sigma h=4n+2, \cos A=0, \sin A=\pm 1.$$

$$S = \sin(h_1\alpha - h_2\beta) \sin(h_2\alpha + h_1\beta) \sin h_3\gamma.$$

$$(3) \Sigma h=4n\pm 1, \cos A=\pm \frac{1}{\sqrt{2}}, \sin A=\pm \frac{1}{\sqrt{2}}.$$

$$S\sqrt{2} = -1.688 + \cos(h_1\alpha - h_2\beta) \cos(h_2\alpha + h_1\beta) \cos h_3\gamma \\ + \operatorname{tg} A \sin(h_1\alpha - h_2\beta) \sin(h_2\alpha + h_1\beta) \sin h_3\gamma.$$

The intensities of the lines are then calculated from the formula (3). In calculating these values we must remember that when  $h_1$  and  $h_2$  are unequal  $S_{h_1, h_2, h_3}$  will be different from  $S_{h_2, h_1, h_3}$  and must be calculated separately.

Having to deal with three parameters, an accurate determination merely by means of the intensity calculations is not a very easy matter. After considerable work we found that the values  $\alpha=20^\circ$ ,  $\beta=20^\circ$ ,  $\gamma=72^\circ$  give a very satisfactory agreement between observed and calculated intensity distribution.

In the case of powellite the metallic atoms are not so dominating, and therefore the intensities in this case are more sensitive to variation of the parameters of the oxygen atoms. Although the parameters undoubtedly are somewhat different for the two minerals, we have used the same parameter for powellite. The observed and calculated intensities are given in Tables VI. and VII., and are perhaps better seen from figs. 12 and 13.

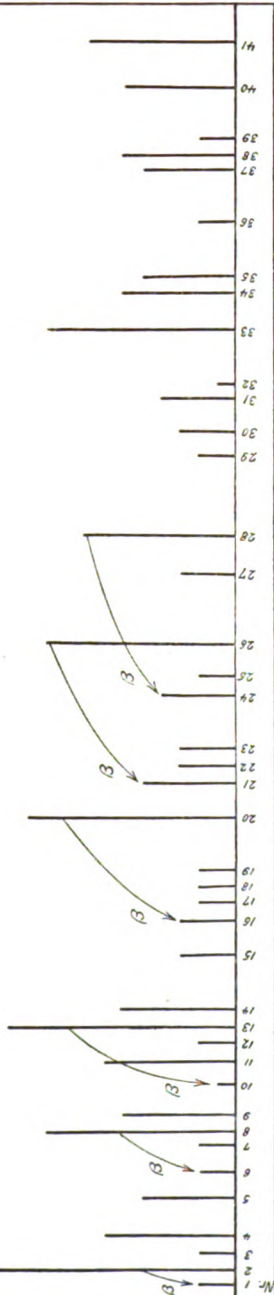
We notice that the intensity distribution found theoretically is essentially the same as that observed, and we are undoubtedly dealing with the right type of lattice.

The parameter values are probably near to the true ones, but we have not gone further in the very laborious work of improving the values by means of the intensity calculations.

In trying to obtain exact parameter values the difficulties met with are not merely due to the laborious calculation work, but they are partly due to the fact that we do not know exactly the accuracy of our fundamental theoretical formulæ. Thus, if the lattice is built of ions and not of neutral atoms, the scattering power (reflecting power) is not proportional to the atomic number. To the first approximation this might be accounted for if in the case of a negative ion we add to and for positive ions subtract from the atomic number so many units as the ion contains free elementary charges. But even then the formulæ can only give the intensities with a certain approximation.

# Scheelite $\text{CaWO}_4$

*Observed Lines*  
*Intensities estimated*



*Intensities calculated*  
*for  $K_\alpha$*

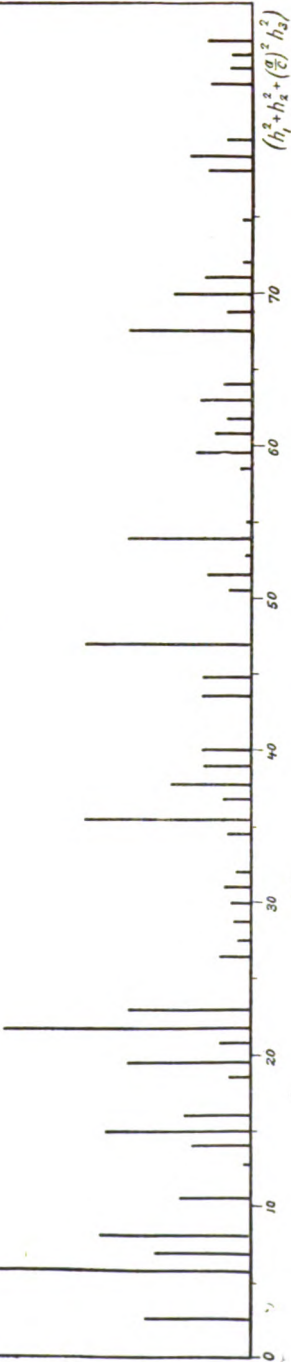
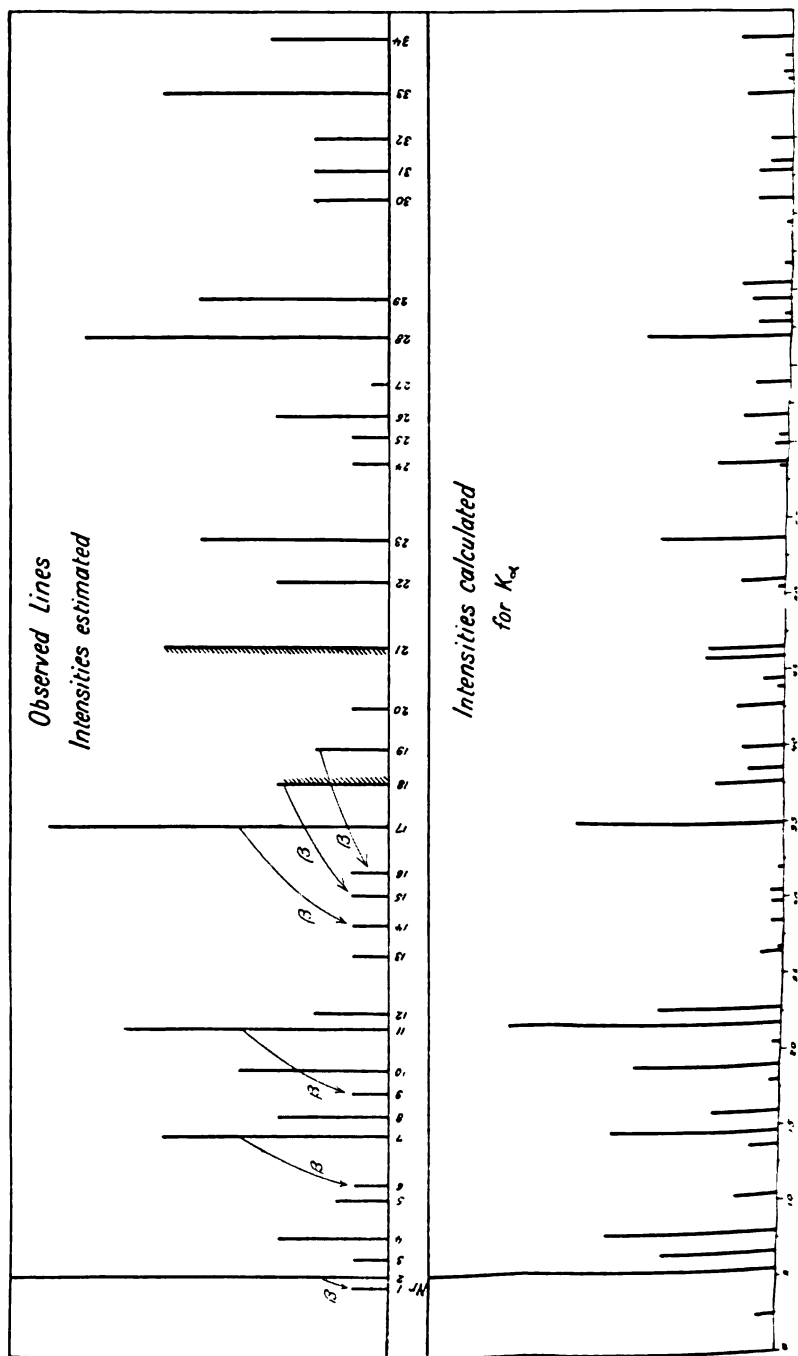


Fig. 13.

Powellite  $\text{Ca Mo O}_4$



Perhaps the most serious incompleteness of the formula results from the fact that the electrons are not united in a space small as compared with the dimensions of the elementary lattice, and according to the distribution of electrons the way in which the intensity varies with  $\phi$  for different sorts of atoms will be different.

We can therefore at present hardly push things further than to obtain a theoretical reproduction of the typical features of the intensity distribution.

In the case of scheelite a number of intensity measurements were made by means of the Bragg ionization method, and as a check we have calculated the intensities by means of our intensity formula.

The result of this comparison is given in Table VIII., and we notice that the agreement is good.

TABLE VIII.

Refl. plane.	Indices .....	4.0.0	8.0.0		
(100)	I { obs. ....	1	0.3		
	cal. ....	1	0.44		
	Indices .....	0.0.4	0.0.8		
(001)	I { obs. ....	1	0.2		
	cal. ....	1	0.2		
	Indices .....	2.2.0	4.4.0	6.6.0	
(110)	I { obs. ....	1	0.4	0.2	
	cal. ....	1	0.1	0.1	
	Indices .....	2.0.2	4.0.4	6.0.6	
(101)	I { obs. ....	1	0.44	0.22	
	cal. ....	1	0.36	0.17	
	Indices .....	1.1.1	2.2.2	3.3.3	4.4.4
(111)	I { obs. ....	1	0	0.2	0.9
	cal. ....	1	0	0.1	0.5

Before arriving at this final solution we have tried a considerable number of other possibilities, and we may here mention the following:—

(1) The oxygen atoms are divided in two groups of 16. One group is associated with Ca, one with W, so that the lattice is formed by groups O—M—O, where M is the metal atoms, and where the axis is parallel to the *c*-axis. The lattice, however, has too high symmetry, and the planes for which  $h_2=0$  and  $h_1, h_2$  even give a too large intensity relative to other planes.

(2) The oxygen atoms are placed on horizontal lines [100] and [010] through the Ca-atoms. This case is derived from the general formula (11) by putting  $\alpha=\beta$  and  $\gamma=0$ .

The symmetry would be too high, the ratio  $c/a$  would be smaller than unity, and the intensity of reflexions like (004) (008) too strong.

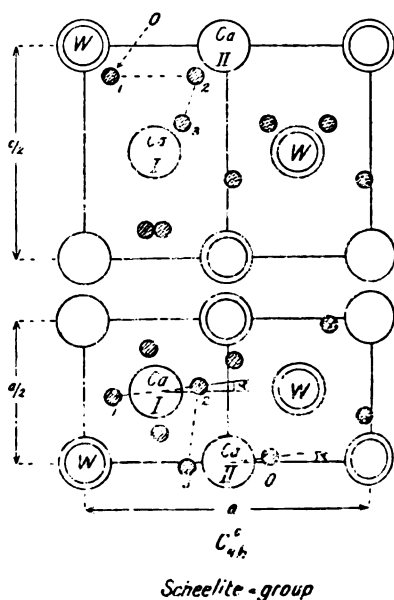
(3) The oxygen atoms are placed on diagonal axis [110] and [1-10] through the centres of symmetry. This case is derived from (11) by putting  $\alpha = -\pi/4$ ,  $\gamma = -\pi/4$ . Symmetry too high, the reflexion from (004) too weak and that of (008) too strong.

(4) The oxygen atoms are situated on the diagonal planes (110) (1-10). This case corresponds to  $\beta = 0$ . Apart from the fact that the symmetry is too high, this arrangement for  $\alpha = 20^\circ$ ,  $\gamma = 70^\circ$  gave a better agreement than the three previous cases. For lines with even indices we obtain a satisfactory intensity distribution, but not for lines with odd indices. Thus the intensity for the plane (311) came out too weak by calculation.

#### Atomic Dimensions.

§ 10. If we regard the atoms as spheres in contact, the lattice may permit the following contacts:—Each oxygen

Fig. 14.



atom (2) makes contact with one W atom and 2 Ca atoms (I and II, fig. 14).

If we regard the oxygen atoms to exist as negative ions with a large "radius," the oxygen atoms may be mutually in contact.

One oxygen atom (2) may probably be in contact with two other oxygen atoms (1, 3, fig. 14).

The centre distances are determined by the following formulæ :

$$\left. \begin{aligned} \text{O}-\text{Ca (I)} &= a \sqrt{l^2 + m^2 + \kappa^2 n^2} \\ \text{O}-\text{Ca (II)} &= a \sqrt{(\tfrac{1}{4}-l)^2 + (\tfrac{1}{4}+m)^2 + \kappa^2(\tfrac{1}{4}-n)^2} \\ \text{O}-\text{W} &= a \sqrt{(\tfrac{1}{4}-l)^2 + (\tfrac{1}{4}-m)^2 + \kappa^2(\tfrac{1}{4}-n)^2} \\ \text{O}_1-\text{O}_2 &= 2a \sqrt{l^2 + m^2} \\ \text{O}_2-\text{O}_3 &= a \sqrt{(2l-\tfrac{1}{4})^2 + (2m+\tfrac{1}{4})^2 + \kappa^2(2n-} \end{aligned} \right\} . \quad (12)$$

where  $\kappa = \frac{c}{a}$ .

The parameters previously used for the intensity calculations were :

$$l = 0.111, \quad m = 0, \quad n = 0.2.$$

These values give :

$$\begin{aligned} \text{O}-\text{Ca (I)} &= 2.415 \text{ \AA.}, \\ \text{O}-\text{Ca (II)} &= 2.201 \text{ ,, } = \text{O}-\text{W}, \\ \text{O}_1-\text{O}_2 &= 1.65 \text{ ,,} \\ \text{O}_2-\text{O}_3 &= 2.53 \text{ ,,} \end{aligned}$$

As we see, the centre distances between O and Ca and between pairs of oxygen atoms do not come out exactly equal. Now we cannot be sure that they really are equal, but the difference of centre distances is so small that it is possible to make them equal by small modifications of the parameters. The parameters should then fulfil the following conditions :

$$\left. \begin{aligned} \text{O}-\text{Ca (I)} &= \text{O}-\text{Ca (II)}, \\ \text{O}_1-\text{O}_2 &= \text{O}_2-\text{O}_3. \end{aligned} \right\} . \quad (13)$$

These conditions give two equations between three parameters. To obtain a third condition we assume that the oxygen atoms exist in the form of negative ions, and that the diameter is about the same as found in the case of zircon.



Putting the centre distance  $O-O=2.25$ , the conditions (13) give for the parameters :

$$\begin{aligned} l &= 0.151, & \alpha &= 28^{\circ}.4, \\ m &= 0.007, & \beta &= 25^{\circ}.9, \\ n &= 0.170, & \gamma &= 61^{\circ}.3. \end{aligned}$$

These parameters give the following dimensions of the ions of scheelite :

$$\begin{aligned} \rho_O &= 1.125 \text{ \AA.}, \\ \rho_{Ca} &= 1.11 \text{ ,,} \\ \rho_W &= 1.04 \text{ ,,} \end{aligned}$$

If we apply the same parameter values to powellite, we obtain :

$$\begin{aligned} O-Ca(I) &= O-Ca(II) = 2.235, \\ O_1-O_2 &= O_3-O_4 = 2.235, \\ O-Mo &= 2.15, \end{aligned}$$

$$\begin{aligned} \text{and} \quad \rho_O &= 1.12 \text{ \AA.}, \\ \rho_{Ca} &= 1.12 \text{ ,,} \\ \rho_{Mo} &= 1.03 \text{ ,,} \end{aligned}$$

Since these results were obtained, investigations on the structure of other members of the scheelite group have been continued at my laboratory. The structure of  $BaWO_4$ ,  $BaMoO_4$ ,  $PbWO_4$ , and  $PbMoO_4$  has been studied by Mr. Alf Refsum by means of the powder method. He finds that all of them have the same structure as scheelite, and the parameters previously used for scheelite give a good agreement between calculated and observed intensities for the whole group of minerals. Details will be given in a separate paper.

The parameters which we have derived by means of the conditions of contact do not differ much from those used for the intensity calculations. We can therefore take it for granted that these somewhat modified parameters would also give a satisfactory agreement between observed and calculated intensities.

If the parameters finally found are correct, it would mean (as  $m \neq 0$ ) that the oxygen atoms are not placed exactly in the planes (100) and (010) through the Ca-atoms, but in planes forming an angle  $\phi$  with these planes (see fig. 14), where

$$\operatorname{tg} \phi = \frac{m}{l} = 0.0465,$$

$$\phi = 2^{\circ} 7.$$

When these "contact" conditions are fulfilled, the lattice, regarded as a system of spheres, should be very stable.

Each W-atom is surrounded by 4 O-atoms, whose centres are placed at the corners of a tetrahedron, which is somewhat compressed in the direction of the *c*-axis.

Each Ca-atom is in "contact" with 8 oxygen atoms, and each oxygen atom touches two Ca-atoms, one W-atom, and two other oxygen atoms.

In conclusion I wish to express my sincere thanks to Mr. Egil A. Hylleraas for his most valuable assistance in connexion with this work.

Physical Institute,  
University, Oslo.  
October 1925.

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CV. *The Orientation of the Oxygen Molecule in a Magnetic Field.* By L. C. JACKSON, M.Sc., Ph.D., A.Inst.P., "1851 Exhibition" Senior Student \*.

ACCORDING to the quantum theory, as developed by Pauli, Sommerfeld, Landé and others, an atom or a molecule possessing a magnetic moment, when placed in a magnetic field, cannot take up any arbitrary orientation with regard to the direction of the field. It can take up only a discrete number of possible orientations determined by certain quantum restrictions. This theory of spacial quantization has been tested and confirmed experimentally by Gerlach and Stern †. Their classical experiments are so well known that any detailed description is unnecessary here. It may merely be mentioned that a very narrow stream of atoms produced by boiling various metals (Ag, Cu, Tl, etc.) is allowed to pass through a very non-homogeneous magnetic field and to fall on a glass plate on which a visible deposit is eventually formed.

The effect of the magnetic field is to split up the stream of atoms into as many separate streams as there are possible quantum orientations for the atom in its particular state. Thus it was predicted and verified that a stream of silver

\* Communicated by the Author.

† Stern, *Zeits. für Phys.* vii. p. 249 (1921); Gerlach & Stern, *ibid.* viii. p. 110 (1921); ix. p. 349 (1922); Gerlach & Cilliers, *ibid.* xxvi. p. 106 (1924); Gerlach & Stern, *Ann. der Phys.* lxxiv. p. 673 (1924); Gerlach, *ibid.* lxxvi. p. 163 (1925).

atoms existing in a singlet 's' state, corresponding to a magnetic moment equal to one Bohr magneton, would be split up into two streams equally disposed on either side of the zero position. The separation of the streams, which is inversely proportional to the mass of the atom and the square of its velocity, was small in Gerlach and Stern's experiments, of the order of a fraction of a millimetre. The experiments are moreover very difficult. One might therefore consider whether the experiment would be possible with some other material which would give a much larger separation of the component streams. If now a jet of oxygen at atmospheric temperature and at little more than atmospheric pressure were sent through a non-homogeneous magnetic field as in Gerlach and Stern's arrangement, then neglecting for the moment, *merely for purposes of argument*, the effect of the collisions between the molecules on their orientations, one would expect theoretically a very large separation. Thus, taking the velocity in question as that of the jet as a whole, the separation to be expected between the component streams would be of the order of 3 centimetres in place of 0.01 mm.\* as in Gerlach and Stern's observations for the same values of the length of path in the magnetic field and of  $dH/dx$ . The stream would probably be split up into three separate streams, a central undeviated one and two equidistant ones on either side (2.0.2) corresponding to a triplet 's' state. Such an experiment could readily be carried out if some means could be found of observing the form of the oxygen stream. How this can be done will be described later.

The proposed experiment differs from that of Gerlach and Stern in two important respects: in the latter, atoms passed through a region of high vacuum while subject to the influence of the magnetic field, so that they passed through without experiencing any collisions, whereas in the other case the oxygen molecules would collide many times while in the magnetic field, and also one would now be dealing with molecules, whereas Gerlach and Stern's observations were carried out, with some possible doubtful exceptions, with atoms. The former difference is of course a fundamental one and the proposed experiment becomes, not one to test the theory of spacial quantization (that can be taken as proved by Gerlach and Stern's experiments), but one to determine the effect of the collisions between the molecules on the orientations taken up by the latter.

\* Stern, *Zeits. für Phys.* vii. p. 249 (1921).

The fact that one is now dealing with molecules and not with atoms is an important one, but in the present state of the theory it would be difficult to state definitely whether it really brings in a fundamental difference.

Let us now consider what may be the effect of the collisions in the proposed experiment. One may take it as certain that during a collision the quantum orientations are completely disturbed. If one made the (improbable) assumption that the molecule after the collision returned to the same orientation which it possessed before, one would expect that the oxygen jet would be split up into separate jets but that the separations of the latter would be less than the theoretical value by a factor depending on the ratio of the duration of the collision to the time in the mean free path. Since the time in collision is short compared with that in the mean free path, the effect of the magnetic field should, on this view, be still easily observable.

If, on the other hand, one makes the usually accepted assumption that all the possible quantum orientations are equally probable so that, after collision, the molecule can take up any one of them, one would expect that the experiment would give a null result if the length of path in the magnetic field were large compared with the mean free path. The molecule would then have passed through all the possible quantum orientations provided that a sufficient number of collisions took place in the magnetic field and the resultant component of the magnetic moment of the molecule in the direction of the magnetic field would be zero. It may be pointed out that the equality of the probabilities of the possible quantum orientations though generally accepted is in reality an assumption. The approximate equality in intensity of the deviated lines in Gerlach and Stern's photographs is in agreement with this idea, since it shows that the various quantum orientations are present in equal numbers. Since, however, collisions do not occur in the magnetic field in Gerlach and Stern's arrangement, their experiments do not give any information as to the distribution among the possible orientations when collisions do occur.

If the proposed experiment were to give a null result, it could be interpreted as showing that the assumption of the equality of the probabilities of the various quantum orientations is justified. If, however, a positive result were obtained many factors would have to be considered before the actual meaning of the result could be stated. Oxygen would seem to be a suitable substance for the experiment, since it certainly possesses a magnetic moment and because

the quantities to be observed, apart from the effect of the collisions, are so large.

The experiment now to be described was carried out about two years ago, before the publication of any of Gerlach's later results. The publication of the observation has been unavoidably delayed by various circumstances, and the theoretical side of the question of spacial quantization has advanced notably since the experiment was carried out. It was, however, thought to be of sufficient interest to warrant publication now.

### *Experimental details.*

In a lecture at the Royal Institution \* Sir James Dewar showed some very beautiful examples of the use of soap-films as detectors of the forms and movements of gaseous jets. If a jet is allowed to impinge obliquely on a soap-film attached to a circular ring of wire or to the end of a wide tube, a system of two beautifully coloured stationary vortices is produced. If now light from an arc lamp is reflected from the soap-film and allowed to fall on a screen some distance away, an enlarged image of the vortex system can be obtained. The point of impact of the jet on the film and the nearly straight line, dividing the vortices from one another, which shows the direction of the incident jet, both show up well and can be focussed quite sharply. If now a change takes place in the position or the form of the jet, this is immediately obvious through a change in the image of the point of impact and in the vortex system. In the publication quoted above is given a large number of photographs of such vortex systems on soap-films, figs. 25 and 31 showing the effect produced under the conditions of the experiment here described.

Such a soap-film was used by Dewar to demonstrate the paramagnetic properties of oxygen by the deflexion of a jet of the gas in a magnetic field. A jet of oxygen was passed between the conical pole pieces of an electromagnet and allowed to fall on to the soap-film. On switching on the current in the electromagnet, the jet was pulled down into the stronger parts of the field and this was immediately seen by the change in the vortex system. The apparatus used is shown in fig. 46 of the paper † already referred to.

This apparatus, after being modified to suit requirements, was used in the present experiment. The pole pieces were

\* Proc. Roy. Inst. xxiv. part 1.

† Dewar, *loc. cit.*

replaced by ones having the same shape as those employed by Gerlach and Stern. Oxygen from a large aspirator arranged to deliver a stream of gas at constant pressure was passed through a fine glass jet suitably arranged with regard to the pole pieces. The stream of oxygen was adjusted as nearly as possible parallel to the edge of the wedge-shaped pole piece. The pressure of the oxygen was so arranged that the velocity of the jet was generally about 15 metres per second. The jet impinged on a soap-film attached to a ring of platinum wire about one inch in diameter placed just outside the field. The image of the film produced on the screen was about three feet in diameter, so that, since a shift of one centimetre of the point of impact of the jet could be readily observed in the enlarged image on the screen, a shift of about 0.3 mm. or rather less of the actual jet could be detected.

The vortex system and the point of impact of the jet on the film were carefully watched as the current was switched on. *In no case was any change in the form of the point of impact observable.* The jet did not, within the limits of fineness of the observations, split up into separate streams nor did it broaden in the direction of  $dH/dx$ . The observation was then repeated many times, changing all the variable quantities in succession. Considerable alterations in the velocity of the jet and in the length of path in the magnetic field were made. The current through the electromagnet was increased from a small value up to as much as 15 or 20 amperes for a short time, but in no case was any positive result observed. The actual value of  $dH/dx$  was not measured, but judging by the field strength obtainable it seemed certain that the largest value of  $dH/dx$  could not have been less than one-tenth of that in Gerlach and Stern's observations. The "theoretical" separation of the component jets for this value of  $dH/dx$  would be easily observable.

This null result is in agreement with the assumption of the equal probability of the possible quantum orientations, and, after considering the various factors which might influence a positive result if such occurred, it may be said that the interpretation of the experiment is probably that the oxygen molecule can after collision take up any one of the possible quantum orientations, passing eventually through them all.

A precise statement of the significance of this result cannot, however, be made until a satisfactory theory has been put forward for the mechanism of the collision of

atoms and molecules in a magnetic field. The result of the experiment described above is now published in the hope of attracting attention to this difficult but important problem.

The experiment was carried out in the Davy-Faraday Laboratory of the Royal Institution, and my thanks are due to the Director, Sir W. H. Bragg, for placing the necessary facilities at my disposal.

The Davy-Faraday Laboratory,  
20 Albemarle Street,  
London, W. 1.  
January 7th, 1926.

CVI. *On the True Signification of Fizeau-Zeeman's Experiments.* By CHARLES L. R. E. MENGES\*.

THE purpose of the present communication is to discuss the signification of the result obtained in a former paper of the writer†. I have shown that the *usual interpretation* of Fresnel-Fizeau's experiment is essentially erroneous on account of two subtle errors, which depend on each other and which we formerly unconsciously introduced. It seems I have not sufficiently emphasized the importance of my correct interpretation, as it was misunderstood.

The development and signification of Einstein's Relativity Theory is treated by Professor Dr. J. D. van der Waals, jr., in a very interesting way in two volumes‡. The first one, issued in 1921, being an introduction to the second one, deals with those points, which, according to the author, lead to Einstein's theory. Fresnel's coefficient and Fizeau's experiment are discussed, obviously with the intention to refer thereto in the second volume in the usual sense as being the decisive experimental confirmation of Einstein's theory. However, in the second volume the reference expected is not to be found.

That second volume appeared in 1923. In the meantime, it resulted from my paper on Fresnel's coefficient § that the

\* Communicated by the Author.

† "On Kinematics," Phil. Mag. xlix. p. 597 (March 1925).

‡ Dr. J. D. van der Waals, jr., 'Over den Wereldether' (1921); 'De Relativiteits-Theorie' (1923); 'De Erven F. Bohn, Haarlem.

§ *Comptes Rendus*, clxxv. p. 574 (1922).

true interpretation of Fresnel-Fizeau's experiment is essentially different from that formerly generally attributed to it. Professor van der Waals's opinion is obviously that the said experiment can no longer be regarded as decisive between Einstein's theory and the older theories and that it may be left out of consideration now.

Apparently this is also the actual prevailing opinion, for Fizeau's experiment was not even mentioned in last year's extensive discussion on Professor Dayton C. Miller's results obtained on Mount Wilson in repeating Michelson and Morley's so-called æther drift experiment. According to a communication from Professor Einstein to "Science Service"\*, he admits now that his theory rests essentially on Michelson and Morley's experiment only, therefore he likewise abandons what he himself repeatedly stated to be the "*experimentum crucis*" or decisive experiment for his theory.

I cannot share that new opinion, as if Fizeau's experiment had no longer any importance in the matter now. The immediate result of Fizeau's experiment is quite certain; in this respect it very much surpasses Michelson and Morley's experiment. This depends on the velocity of the Earth in an hypothetical way; that velocity is a circumstance outside the laboratory, quite beyond our control, not changeable, not reversible. In Fizeau's effect, on the contrary, its main cause and all details are well controllable, exactly determinable, and they may be changed and reversed at will.

Professor Dayton C. Miller claims a result for his repetition of Michelson and Morley's experiment, which is only 30 per cent. at most of the calculated effect. Certainly, Professor Miller observed an effect of the said magnitude, but the question remains: is it due to the alleged æther wind? There is no incertitude of this kind in Fizeau's experiment. This experiment therefore maintains its character as "*experimentum crucis*" (decisive experiment) quite independent of what it proves or disproves, which depends on the interpretation of the result.

For more than a century Fresnel's formula and Fizeau's experiment concerning light transmitted by moving substances formed a problem which scientists have tried to solve in different ways. The main point in the problem is the fact that a solution resting on certain well-established

\* 'Science,' lxii. Supplement, p. 8 (July 31, 1925).



bases (see below) could not be obtained. Therefore, the generally admitted inferences were :—

1. The solution of the problem on said bases is impossible; to solve the problem any particular hypothesis, suitable to lead to the solution, must be added.

2. The said bases are only approximately, but not essentially, true.

In this sense the last alleged solution is that by means of Einstein's theory, which was originally given by Professor von Laue.

That formerly admitted insight in the question is now wholly null and void in consequence of my solution.

The fact is : *on the said bases, and without introducing any particular hypothesis, I established the formula for the experiment.*

Any formula may be made to fit a particular experiment by means of a suitable chosen so-called constant. However, under different circumstances, it generally will not suit. Only when the formula is correctly based on true general physical laws, will it give with the same constant correct results over a wide range. Especially when the formula proves to be true under the most different circumstances—which is just the case here, as I point out below—then the laws as well as the constant are well confirmed.

To test the validity of physical or other laws, the well-known way is to calculate, according to those laws, the result of experiments and compare it with the actual experimental result. Of course, the calculation must be correct, that is, *all formulae used must be strictly consistent with the laws to be tested.*

Unconscious deviations from this logical law led to the hitherto encountered difficulties. It is by strictly avoiding such deviation that I arrived at *quite new results*, free from difficulties, free from any old or new doubtful hypothesis.

I emphasize this to avoid my communication being mistaken as analogous with the attempts to refute Einstein's theory, which all mainly aim at reverting to older theories, as, for instance, in Professor E. Gehrcke's controversy with Dr. M. Born\*, and in Professor P. Lenard's polemic pamphlets against Einstein's theory.

In the question I here discuss, it is the old idea of a "dragging coefficient" which led to Einstein's theory. *According to my new result the true interpretation of the experiment is radically different to that old idea.* As a

\* 'Die Naturwissenschaften,' i. pp. 62, 92, 170, 191, 338.

consequence then, it follows that Einstein's theory cannot be maintained.

In the same way I treat electromagnetic theory in my books '*Nouvelles vues Faraday-Maxwelliennes*' and its '*Supplément—Sur la Propagation de la Lumière*' (Gauthier-Villars & Cie, Paris, 1924). I refer thereto concerning the connexion of the actual subject with electromagnetic theory.

I established my formula for the experiment on light transmitted by moving substances, namely for the actual observable shift of the interference fringes, on the following bases :—

1. The laws of Kinematics. For the case in question the result of the velocity  $v$  and another velocity  $\mp w$  in the same direction is the velocity

$$u = v \mp w.$$

2. The aforesaid laws are generally true, without any exception ; they hold also when one of the velocities, say  $v$  is  $c$  = the velocity of light in vacuo ; the velocity obtained by compounding  $c$  with  $\mp w$  is

$$c' = c \mp w.$$

3. The refractive index of a substance is the ratio of the velocity of light outside the substance to the velocity of light inside that substance, both velocities calculated relatively to the substance, according to 1 and 2.

The formula I established on said bases (see my Phil. Mag. paper, and, for further details, my books above referred to) is confirmed by Professor P. Zeeman's experiments\*. I particularly mention Zeeman's experiments, as his results are undoubtedly the most accurate so far obtained. *They confirm my equation practically to 100 per cent.* Moreover, his experiments do not only concern moving water, as in former experiments, but also quartz and moving glass. The experimental results with such different substances being in so close accordance with my formula, *they form the decisive confirmation of the fundamentals, as stated under 1, 2, and 3.*

*The validity of 1 is the immediate disproof of the formula for compounding velocities in Einstein's theory.*

*The validity of 2 is the immediate disproof of what Einstein's theory admits as its basis.*

\* P. Zeeman, *Verslagen Akadem. Amsterdam*, xxi. p. 245 (1914); xxiv. p. 18 (1915); xxvii. p. 1453 (1919); xxviii. p. 1462 (1919); xxix. p. 1252 (1920).

CVII. *The Scattering Powers of Calcium and Fluorine for X-Rays.* By R. W. JAMES, M.A., Senior Lecturer in Physics, Manchester University, and J. T. RANDALL, B.Sc.\*

1. *Introduction.*

IN determining the arrangement of the atoms in a crystal structure from a consideration of the intensities of the X-ray spectra reflected from the different sets of atomic planes, it is necessary to make allowance for the relative diffracting powers of the various atoms. In many cases it has been sufficient to ascribe to each atom a diffracting weight proportional to its atomic number, and to the number of electrons contained in it. This, however, can only be approximately correct, for the scattering power of an atom must be a function of the angle of scattering. The electrons which contribute to the scattered beam are distributed, in each atom, through a volume whose dimensions are of the same order of magnitude as the distance between the atomic planes and the wave-length of the X-rays used in the investigation. Thus the contributions of the different electrons, in any direction, to the scattered beam will differ in phase, and the phase-difference will depend on the angle of scattering. We may, in fact, write the scattering power of the atom as  $F$ , where

$$F = Zf(2\theta, \lambda).$$

$Z$  in this expression is the number of electrons contained in the atom or ion;  $f(2\theta, \lambda)$  is a function of the angle of scattering  $2\theta$  and of the wave-length  $\lambda$  of the rays used, which will approach unity for small values of  $\theta$  and will, in general, decrease as  $\theta$  increases. The quantity  $F$  will depend, therefore, not only on the total number of electrons in the atom, but on their arrangement, and on the angle of scattering. If we consider, for example, two ions both containing the same number of electrons, but one having a considerably greater nuclear charge than the other, so that its electrons are pulled in much more closely, the value of  $F$  for the two ions will be nearly the same at small angles of scattering, but will fall off much more slowly as  $\theta$  increases for the compact ion than for the more loosely-bound one. Thus the ratio of the diffracting powers of the ions will not remain constant as the order of the spectra increases, and

\* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

structure-amplitudes calculated on the assumption that it does so will be incorrect.

In determining the simpler structures, where a large amount of information can be obtained from symmetry, and where there are only one or two kinds of atom present, this is of little importance. It becomes highly important, however, in the more complex inorganic crystals, where most of the information has to be derived from consideration of intensities, and where three or four different kinds of atom may be present. For progress in determining these structures it is of the first importance to get some idea of the value of the factor  $F$  for as many atoms as possible. The importance of the factor  $F$  was first pointed out by Darwin \*, and by Compton †, in theoretical papers on the intensity of reflexion of X-rays. An experimental study of the  $F$  factor for Na and Cl has been made by W. L. Bragg, James, and Bosanquet ‡, and the value of  $F$  for a number of ions has been calculated by Hartree § assuming the forms of the electronic orbits calculated by him from spectral terms. Hartree's  $F$  values, with certain modifications, were used by James and Wood || in determining the structure of barium sulphate, and in this crystal in particular it was assumed that the diffracting power of the loosely-built oxygen ion, with its small nuclear charge, would fall away relatively far more rapidly as the angle of scattering increases than that of the compact Ba atom with its nuclear charge of 58. Some assumption of this kind appeared to be necessary to explain the observed spectra at all.

## *2. The relative Scattering Powers of Potassium and Chlorine.*

The values of  $F$ , both experimental and calculated, depend, however, on the application of certain formulæ whose theoretical basis is not entirely secure, and it would evidently be interesting to obtain direct experimental proof that the relative diffracting powers of two ions or atoms do change with the angle of scattering in the sense assumed. Suppose we have a crystal containing two different ions, each having the same number of electrons, and that in certain spectra the contributions from two ions are always

\* Phil. Mag. xxvii. p. 315 (1914).

† Phys. Rev. ser. 2, ix. p. 29 (1917).

‡ Phil. Mag. xlii. p. 1 (1921); xliv. p. 433 (1922).

§ Phil. Mag. l. p. 289 (1925).

|| Proc. Roy. Soc. A. 109, p. 598 (1925).

exactly out of phase. The amplitudes of the spectra will then be proportional to the difference of the  $F$ 's for the two ions. If the  $F$ 's are exactly equal and opposite for some angles of scattering, they ought not to be so for other, higher, angles of scattering. Thus by examining spectra of this type we can test the assumption directly without using any doubtful theories.

Sylvine,  $KCl$ , appears to be a suitable crystal of this type. It has the rock-salt structure and contains the ions  $K^+$ ,  $Cl^-$ , each of which has 18 electrons. All the spectra in the crystal having 3 odd indices have structure-amplitudes of the type  $(K-Cl)$ ; thus by observing such spectra at a variety of glancing angles it ought to be possible to see whether the scattering powers are equal at all angles. As a matter of fact, the crystal is not a very suitable one. The nuclear charges are 19 and 17, so that the scales of the electronic orbits will not differ greatly. The intensities of the spectra will be proportional to  $\left(\frac{F_K - F_{Cl}}{F_K + F_{Cl}}\right)^2$ , or nearly so, since the crystal approaches the mosaic type, and will therefore always be very small, since  $F_K$  and  $F_{Cl}$  will not differ very much at any angle. As a matter of fact, a careful search failed to reveal any spectra of the type  $(K-Cl)$ . It must be remembered, however, that we should not expect much difference between the two  $F$ 's except at high angles of scattering, when even the normal spectra are weak, so that a difference of the amount to be expected theoretically might well have escaped detection with the X-ray intensity at our command. To get definite results, we require two ions whose  $F$ 's are likely to differ more than those of  $K$  and  $Cl$ , and, for this reason, a study of the spectra of fluorite,  $CaF_2$ , has been made.

### 3. Discussion of the case of Fluorite.

The structure of fluorite was determined by W. L. Bragg\*. The calcium atoms lie on a face-centred cubic lattice. If the face-centred unit cube be divided into eight smaller equal cubes, the fluorine atoms lie at the centres of each of these. The structure-amplitude  $S_{hkl}$  for the spectrum  $(hkl)$  is given by

$$S_{hkl} = Ca \cos \frac{h+k}{2} \pi \cos \frac{k+l}{2} \pi \cos \frac{l+h}{2} \pi \\ + 2F \cos \frac{h\pi}{2} \cos \frac{k\pi}{2} \cos \frac{l\pi}{2},$$

\* Proc. Roy. Soc. A, lxxxix. p 474 (1914).

where  $\text{Ca}$  and  $\text{F}$  are the scattering power of  $\text{Ca}$  and  $\text{F}$  in the direction of the spectrum concerned. They are, in fact, the  $\text{F}$ 's for  $\text{Ca}$  and  $\text{F}$ , but are written in this way for convenience. There are thus only four types of structure-amplitude:—

(a) For all spectra with one odd and two even, or one even and two odd indices,  $S=0$ .

(b) For all spectra with three odd indices,  $S=\text{Ca}$ .

There remain spectra for which all the indices are even, say  $(2m, 2n, 2p)$ ; for these we have

(c) If  $m, n, p$  are all even, or if two are odd and one is even,  $S=\text{Ca}+2\text{F}$ ;

(d) If  $m, n, p$  are all odd, or if two are even and one is odd,  $S=\text{Ca}-2\text{F}$ .

The interesting spectra are those of the type  $S=\text{Ca}-2\text{F}$ . Assuming the calcium and fluorine to be ionized,  $\text{Ca}^{+2}$  will contain 18 electrons, and  $\text{F}^-$ , 10 electrons. Thus, for small angles of scattering,  $S=\text{Ca}-2\text{F}=18-20$ , and the intensity of the spectrum should be a fraction  $\left(\frac{20-18}{20+18}\right)^2 = \frac{1}{361}$  of the normal spectrum of type  $\text{Ca}+2\text{F}$  at the same angle. It should thus be very small, and, indeed, hardly to be detected with the means at our disposal. But the greater nuclear charge of the calcium may be expected to hold the electron structure far more tightly than the smaller charge of the fluorine. In fact, there is reason to believe that the whole structure of 18 electrons lies within a sphere of diameter about 2.1 Å. in the case of calcium, while the 10 electrons of fluorine probably require a sphere of 2.7 Å. diameter to contain them completely. Moreover, we shall expect a much greater concentration of electrons near the centre in the case of  $\text{Ca}$ . Hartree's figures indicate, in fact, that whereas, for  $\text{MoK}_\alpha$  radiation,  $\text{F}$  for  $\text{Ca}^{+2}$  will be still about 12, for a scattering angle of  $60^\circ$ , that for  $\text{F}^-$  will have sunk below 1.

Thus at this angle the value of  $\left(\frac{\text{Ca}-2\text{F}}{\text{Ca}+2\text{F}}\right)^2$  will be  $\left(\frac{5}{7}\right)^2$ , and, thus, spectra found at angles as large as this should be quite strong relatively to the normal.

It was shown by Pealing\* that, while the (200) spectrum † from  $\text{CaF}_2$  was extremely weak, the (600) was much stronger, but no examination of other spectra of the type  $\text{Ca}-2\text{F}$  was

\* Proc. Phys. Soc. Lond. xxxiii. p. 297 (1921).

† These spectra are called (100) and (300) in Pealing's paper. We have referred them to the true unit spacing, 5.47 Å., in which case they become (200) and (600).

made. These results were discussed by Yamada\*, who ascribed them to the correct cause, but based on these two isolated observations rather more than they can carry. In a paper read before the American Physical Society, of which, however, so far as we are aware, only an abstract has appeared, McInnes and Shedlovsky† described some measurements of the intensities of the various spectra from fluorite. They obtained spectra of the type  $\text{Ca} + 2F$ ,  $\text{Ca}$ ,  $\text{Ca} - 2F$ , but they do not seem to have considered these results from the point of view of the present paper.

#### 4. *Experimental Results with Fluorite.*

We have made a series of observations of the absolute intensity of reflexion for a number of different spectra from fluorite. In Table I. the results of the observations are summarized. Two different crystals, indicated by (1) and (2), were used. All the faces were ground with emery-paper, which has the effect in most cases of increasing the intensity of reflexion. The intensities  $\rho$  are the "integrated reflexions" obtained in the usual manner by rotating the crystal with uniform angular velocity through the reflecting position, and observing the total ionization received by the chamber, correction being made for general radiation.  $\rho$  is expressed in absolute measure‡. The radiation employed was Molybdenum  $K_{\alpha}$  of wave-length  $\lambda = 0.710 \text{ \AA}$ .

The crystals (1) and (2) were both similar in appearance, and showed a considerable amount of blue fluorescence, and the spectra obtained from them are comparable in intensity. In addition, a number of observations were made from a third crystal (3), which was clear and colourless, and appeared to be considerably more warped than the others. The strong spectra from (3) were from 45 to 50 per cent. more intense than the corresponding ones from (1) and (2), and even the weak ones were much stronger. This seems to show that fluorite is some way from being a true mosaic crystal, and that extinction is playing a considerable part in reducing the intensities of the strong spectra. We shall return to this point later.

\* Nagacka Anniversary Volume, p. 121.

† Phys. Rev. ser. 2, xxiii. p. 290 (1924).—(Note added April 22, 1926.) While this paper has been in the press McInnes and Shedlovsky have published this work in much greater detail (Phys. Rev. ser. 2, Feb. 1926, p. 130).

‡ The spectra were all compared directly with the (400) reflexion of NaCl. The absolute intensity of the spectrum for Mo  $K_{\alpha}$  was taken as  $9.4 \times 10^{-5}$ . This number is based on the measurements of Wasastjerna.

TABLE I.

Spectrum.	S.	$\sin \theta$ .	Crystal.	$\rho \times 10^6$ .	$\sqrt{\rho} \times 10^3$ .
(111)	Ca	1124	(1)	124.8	11.18
(113)	"	2153	(2)	43.7	6.63
(333)	"	3372	(1)	12.65	3.56
(555)	"	5620	(1)	2.75	1.67
(339)	"	6459	(2)	1.45	1.18
(220)	Ca+2F	1835	(2)	125.0	11.18
(400)	"	2596	(1)	73.9	8.49
(440)	"	3670	(2)	23.2	4.82
(800)	"	5192	(1)	8.72	2.96
(660)	"	5505	(2)	6.1	2.47
(880)	"	7340	(2)	2.02	1.43
(1200)	"	7788	(1)	2.02	1.43
(200)	Ca-2F	1298	(1)	—	—
(222)	"	2248	(1)	2.03	1.43
(600)	"	3894	(1)	2.43	1.56
(226)	"	4306	(2)	1.62	1.28
(1000)	"	6490	(1)	0.81	0.90

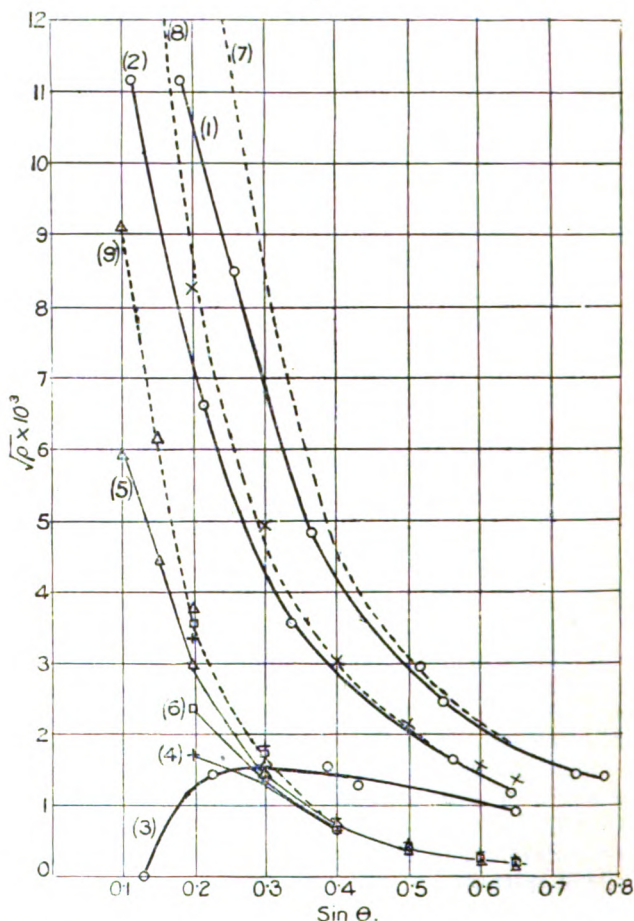
### 5. Discussion of Results.

The figures in column 6 of Table I., giving the square roots of the intensities, are plotted against the sines of the corresponding glancing angles in fig. 1. It will be seen that the points are grouped on three curves, (1), (2), and (3), corresponding to structure-amplitudes Ca+2F, Ca, and Ca-2F respectively. The curve for Ca-2F is very interesting. No definite (200) spectrum could be observed; at the angle of scattering for this spectrum,  $14^\circ 54'$ , the effect of two fluorine ions almost exactly neutralizes that of the calcium ion. The (222) spectrum, on the other hand, at an angle of scattering of  $26^\circ 0'$  is quite appreciable, so that the balance is destroyed at this angle, and (600), (226), (10,00) all appear, the latter at an angle of scattering of  $80^\circ 56'$  being only a little weaker than the (222). Had the ratio of the scattering powers of  $\text{Ca}^{+2}$  and  $\text{F}^-$  remained constant as the angle of scattering increased, the spectrum (10,00) would have had an intensity of not more than one per cent. of that of the (200). It is quite evident that, for the higher angles of scattering, either the effect of two



fluorine ions is much less than that of one calcium ion, or that of one calcium ion is much less than that of two fluorine ions. Taking the three curves together, it is evident that the former alternative is the correct one. The three curves

Fig. 1.



To avoid confusion the separate curves for fluorine are not drawn for the higher angles. Corresponding points on the corrected and uncorrected fluorine curves are indicated by the same symbol. Circles are observed points.

differ widely for small angles of scattering, but converge for the larger ones, so that the intensities for angles of about  $35^\circ$  to  $40^\circ$  are of much the same magnitude whether the

structure factor is  $\text{Ca} + 2\text{F}$ ,  $\text{Ca}$ , or  $\text{Ca} - 2\text{F}$ . The only way in which the results can be explained is by supposing that the F factor for fluorine becomes less and less in comparison with that for calcium as the angle of scattering increases, so that, at large angles, it matters comparatively little whether the effect of the fluorine is added to or subtracted from that of calcium or not. The curves seem to prove, in fact, in a very direct way, apart from any assumptions, that the scattering power of fluorine becomes small at large angles of scattering.

#### 6. *Calculation of Intensity due to Fluorine alone.*

Although there is no spectrum for which the structure-amplitude is due to fluorine alone, it is possible to calculate its effect by combining the other curves. If the crystal were of the ideal mosaic type for which the intensities of the spectra are proportional to the squares of the structure-amplitudes, the square roots of the intensities should be proportional to the amplitudes scattered by the atoms. The difference of the ordinates of curves (1) and (2) divided by two should therefore give the ordinates of the curve on which the intensities of the spectra due to fluorine alone, if such existed, would lie. We could also obtain this curve by subtracting the curve for  $\text{Ca} - 2\text{F}$  from that for  $\text{Ca}$ , and also by subtracting  $\text{Ca} - 2\text{F}$  from  $\text{Ca} + 2\text{F}$ , and the curves obtained in these three ways should agree. Curves (4), (5), and (6) show the fluorine curves obtained in these three ways in the order stated. It will be seen that, while they agree very well for large angles, they are widely divergent for the smaller ones.

The additive law thus breaks \* down, but the manner in which it does so suggests that the crystals used were too perfect to be treated as an ideal mosaic. The strong spectra will thus be much reduced by extinction, or, in other words, the effective absorption coefficient at the reflecting angle will depend on the intensity of the spectrum. The curve (4) was obtained from  $\text{Ca} + 2\text{F}$  and  $\text{Ca}$ , for both of which the spectra are strong at small angles, while for each of the other two curves the  $\text{Ca} - 2\text{F}$  curve was used, for which the increased absorption due to extinction is nearly negligible; and if the extinction is at all strong, we should also expect the difference to be much less for the large angles, since the weaker high-order spectra are but little affected by extinction.

\* This result was also noticed by McInnes and Shedlovsky.

## 7. Allowance for Extinction.

We have tested this idea by trying to make some allowance for extinction. It was shown in the case of rock-salt\*, for which the extinction is probably mainly secondary†, that the effective absorption coefficient for a spectrum of intensity  $\rho$  was  $\mu_0 + \alpha\rho$ , where  $\mu_0$  is the ordinary absorption coefficient when the crystal is not reflecting and  $\alpha$  is almost constant. Suppose that the extinction in the case of fluorite is of this type. On the assumption that the crystal is an ideal mosaic, the integrated reflexion  $\rho$  for a spectrum, occurring at a glancing angle  $\theta$ , and for which the sum of the  $F$  factors for the atoms in one molecule is  $\Sigma F$  ‡, is given by

$$\rho = \frac{N^2 \lambda^3}{4\mu} \cdot \frac{e^4}{m^2 c^4} (\Sigma F)^2 \cdot \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot e^{-BT \sin 2\theta}. \quad (1)$$

In this formula,  $N$  is the number of molecules per cubic centimetre,  $\lambda$  the wave-length of the radiation employed, and  $\mu$  the linear absorption coefficient.

The exponential term makes allowance for the heat-motions of the atoms, while  $e$ ,  $m$ , and  $c$  have the usual significance. We have assumed that  $\mu$  is to be replaced by  $\mu_0 + \alpha\rho$ , where  $\mu_0$  is the ordinary absorption coefficient when the crystal is not reflecting, and have made an estimate of  $\alpha$ .

For this purpose the (111) spectrum was used. This occurs at a small angle, is strong, and is due to Ca alone. The temperature factor, which is not known for this crystal, will in any case be small at this angle and is neglected. There is some uncertainty about  $F$ . But whatever assumption is made about the distribution of the electrons in the  $\text{Ca}^{+2}$  ion, the value of  $F_{\text{Ca}}$  must approach 18 for  $\theta=0$ , and hence, for a small angle of scattering, such as that for (111), we shall probably not make a large error if we assume Hartree's value for  $\text{Ca}^{+2}$ . The value of  $F$  for  $\sin \theta = 0.1124$  is 15.5, and we have used this in the calculation. The value of  $\mu_0$  as measured, using a thin slip of fluorite, is 31.3.

\* Phil. Mag. xlii. p. 1 (1921).

† Darwin, Phil. Mag. xliii. p. 800 (1922).

‡ It is assumed throughout that the "average atoms" are spherically symmetrical, so that  $F$  depends only on  $\theta$  and not on the particular direction of the scattered beam with reference to the crystal axes. This no doubt is only approximately correct for more complicated crystals, but appears to be very nearly the case in simple ionized structures.

The calculated value of  $\rho$  for (111), using this value of  $\mu_0$ , came out to be  $284.5 \times 10^{-6}$ , whereas the observed value is  $124.8 \times 10^{-6}$ . Assuming that the difference is due to extinction, we have

$$\frac{\mu_0 + \alpha\rho}{\mu_0} = \frac{284.5}{124.8} = 2.28,$$

whence, putting  $\mu_0 = 31.3$ ,  $\rho = 124.8 \times 10^{-6}$ , we obtain

$$\alpha = 3.21 \times 10^5.$$

We may call  $\alpha$  the "extinction coefficient." If  $\mu$  is the effective absorption coefficient for a spectrum of intensity  $\rho$ , we may write

$$\mu = \mu_0 + \epsilon \quad \text{where} \quad \epsilon = \alpha\rho.$$

For (111),  $\epsilon = 40.3$ ,  $\mu = 71.6$ , so that the effective absorption coefficient is more than twice the normal one. For the weak (800),  $\epsilon = 2.8$  and  $\mu = 34.1$ ; thus the intensity is very little affected by extinction.

Having obtained this value of the extinction coefficient  $\alpha$ , we can now correct the observed curves by multiplying the ordinates by the corresponding values of  $\sqrt{\frac{\mu_0 + \epsilon}{\mu_0}}$ . In this way, the corrected curves (7) and (8) in fig. 1 were obtained for Ca + 2F and Ca; the corrected curve for Ca - 2F is not distinguishable for the uncorrected one on the scale of the diagram.

From these corrected curves the three fluorine curves were recalculated. These are shown in curves (9) in fig. 1, and it will be seen that the discrepancies for small angles of scattering have nearly disappeared, while the agreement remains good for the larger angles. The crosses in fig. 1 represent the points obtained for Ca from the curves Ca - 2F and Ca + 2F, which are given for comparison with the corrected Ca curve.

Thus the corrected observations are consistent with one another, and support the assumption that the extinction in fluorite is largely secondary\*; that is to say, that the

\* It must be emphasized that the values of the extinction determined in this way are valid only for the particular crystal used. Fluorite is certainly very variable in its degree of perfection. The high values of  $\rho$  from crystal (3) have already been mentioned. At the other extreme, a particularly clear cleavage fragment gave a value  $\rho = 47 \times 10^{-6}$  for (111). After grinding with emery, the same face gave  $\rho = 113 \times 10^{-6}$ .

homogeneous fragments of the crystal mosaic are not large enough to reflect totally the radiation falling on them. There may, however, be some primary extinction, for some of the weak spectra obtained from crystal (3) were stronger than the corresponding ones from (1) and (2), even when the latter have been corrected. It must be remembered, however, that spectra for which the absolute intensity is  $2 \times 10^{-4}$  or less are very difficult to measure accurately, and that very considerable percentage errors in these are possible.

In Table II. we give the values of  $\rho$  for the smoothed observed curves for a series of values of  $\sin \theta$ , together with the corresponding corrected values.

TABLE II.

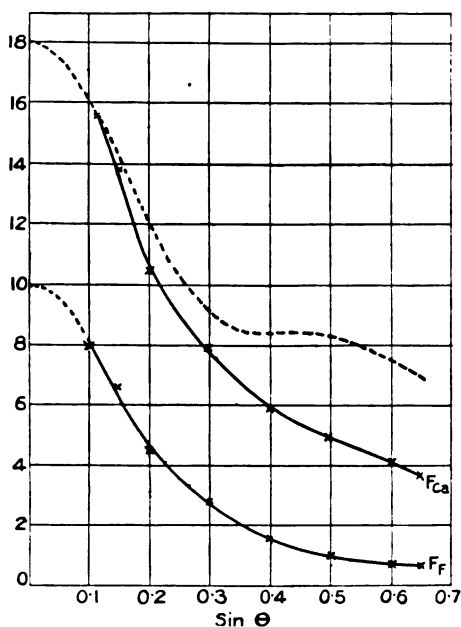
Sin $\theta$ .....	0.1	0.15	0.2	0.3	0.4	0.5	0.6	0.65
Ca+2F $\rho \times 10^6$	—	—	10.59	6.89	4.19	2.96	2.11	1.77
$\rho$ corr.	—	—	15.52	8.41	4.65	3.07	2.16	1.80
Ca $\rho$	11.73	9.33	7.11	4.29	2.89	2.05	1.45	1.23
$\rho$ corr.	18.23	12.84	8.76	4.69	3.01	2.09	1.46	1.24
Calculated from Ca+2F and Ca-2F	—	—	8.39	4.96	3.05	2.16	1.46	1.36
Ca-2F $\rho$	—	0.59	1.26	1.50	1.45	1.24	1.03	0.92
$\rho$ corr.	—	0.59	1.27	1.52	1.46	1.25	1.04	0.92
F								
$\frac{1}{2}\{(Ca+2F) - Ca\}$ $\rho$	—	—	1.74	1.30	0.65	0.46	0.33	0.27
$\rho$ corr.	—	—	3.38	1.86	0.82	0.49	0.35	0.28
$\frac{1}{2}\{(Ca+2F) - (Ca-2F)\}$ $\rho$	—	—	2.33	1.35	0.68	0.43	0.27	0.21
$\rho$ corr.	—	—	3.56	1.72	0.80	0.45	0.28	0.22
$\frac{1}{2}\{Ca - (Ca-2F)\}$ $\rho$	5.86	4.37	2.92	1.39	0.72	0.40	0.21	0.16
$\rho$ corr.	9.11	6.12	3.74	1.58	0.78	0.42	0.21	0.16

### 8. The F Curves for Calcium and Fluorine.

In fig. 2 the F curves for calcium and fluorine are plotted against the sines of the glancing angles. These curves were obtained by substituting in formula (1) of section 7. The

values of  $\rho$  were obtained from the corrected curves for Ca and F; in the case of fluorine, where the curve was obtained in three ways, a mean curve was drawn. The curves are uncorrected for the temperature factor, the value of which is not known for fluorite. Allowance for this factor would make little difference to the curves for small values of  $\theta$ , but would considerably increase the values of F for the larger angles. Hartree's curve for  $\text{Ca}^{+2}$  is given for comparison.

Fig. 2.



The dotted curve is Hartree's curve for  $\text{Ca}^{+2}$ .

It must, of course, be remembered that the curve for Ca is forced to fit Hartree's curve at small angles by the method of correction. The Ca curve falls away much more rapidly than Hartree's curve for moderate angles, and it is unlikely that the temperature factor will account for all the difference. Possibly the cause of the discrepancy is to be sought in the increasing fraction of the incident radiation which at high angles of scattering will undergo Compton scattering, and will therefore probably not take part in the interference.

The calculated values of F uncorrected for temperature factor are given in Table III.

TABLE III.

Sin. $\theta$ .....	0.1	0.15	0.2	0.3	0.3	0.5	0.6	0.65
Ca+ <sup>2</sup> .....	15.8	13.8	10.5	7.9	5.9	4.9	4.1	3.6
F <sup>-</sup> .....	7.9	6.6	4.5	2.8	1.5	1.0	0.70	0.60

9. *Summary.*

(1) The absolute intensities of reflexion have been measured for a series of spectra from fluorite. The structure-amplitudes in the crystal are of three types Ca + 2F, Ca, and Ca - 2F, and the observed spectra are grouped on three corresponding curves.

(2) The spectra of type Ca - 2F are absent or very small for small glancing angles, but become much more important relatively to those of type Ca and Ca + 2F at larger glancing angles. This shows in a direct way that the value of the scattering power F for fluorine becomes less and less important relatively to that for calcium at large angles of scattering.

(3) Curves showing the variation of the square root of the integrated reflexions for the three types of spectra are given. From these curves it is possible to calculate the curve for fluorine in three different ways. The curves so obtained are divergent for small glancing angles, but agree at higher ones. The divergence is ascribed to increased absorption due to "extinction." On the assumption that the extinction is proportional to the observed intensity, a correction is applied which removes most of the difference between the three curves.

(4) The F curves for fluorine and calcium are obtained from the observations, and are compared with those calculated by Hartree.

We wish in conclusion to express our thanks to Prof. W. L. Bragg, F.R.S., for his interest and advice during the course of this work. Part of the apparatus used was purchased by means of a grant from Messrs. Brunner, Mond, Ltd., to whom our thanks are also due.

Manchester University,  
Feb. 8, 1926.

CVIII. *Notices respecting New Books.*

*Higher Mathematics for Students of Engineering and Science.* By F. W. G. BROWN. (Macmillan & Co., 1926. 10s.)

**I**N writing this book the author has had particularly in mind the needs of Engineering Students, and his object has been to deal in a single volume with all the branches of pure mathematics required for an engineering degree. The amount of Calculus and Analytical Geometry given is, however, rather greater than that required by the engineering syllabuses in most universities. The general style of the book is good, and it should prove a welcome addition to the rapidly increasing number of introductory treatises addressed not to the mathematical student, but to those who are concerned only with the applications of mathematics to problems in the various branches of science and industry.

*Vectorial Mechanics.* By L. SILBERSTEIN, Ph.D. Second Edition. (Macmillan & Co., 1926. 10s.)

**THIS** new edition of Dr. Silberstein's important and valuable work, first issued in 1913, differs from the original edition by the inclusion of some Miscellaneous Notes. The first is concerned with a projective or non-metrical generalization of the concept of vector equality. Another contains a concise exposition of the theory of linear vector operators, and the last gives a simplified vectorial deduction of the properties of Euler's angles determining the orientation of a rigid frame.

These new notes add to the usefulness of the volume. The book gives a short but essentially complete exposition of mechanics, and it should also be of value as an introduction to the algebra and analysis of vectors.

*The Theory of Functions of a Real Variable and the Theory of Fourier's Series.* By E. W. HOBSON. Second Edition, revised throughout and enlarged. Vol. 2. (Cambridge University Press, 1926. 50s. net.)

**PROFESSOR HOBSON'S** volume of the Theory of Functions of a Real Variable, which was originally issued in 1907, has now been reissued in two volumes, the first in 1921 and the second in 1926. Almost the whole of the matter presented in the present volume has been rewritten, and a great deal of new material has been added, material based on the investigations of a number of mathematicians in the intervening period. Thus considerable space has been allotted to a discussion of various theories of integration due to Young, Tonelli, and Perron; a full discussion is given of the theories of conventional summation due to Cesàro, Hölder, and Marcel Riesz; F. Riesz's classification of summable functions is also included. A special feature of the volume is the prominence given to the General Convergence Theorem, which is



treated very fully. On this discussion depends the treatment of the convergence of Fourier's series and Integrals given in later chapters. There is also an account of the interesting modern theory of Fourier transforms.

*Matrices and Determinoids.* Vol. 3, Part 1. By C. E. CULLIS. (Cambridge University Press, 1925. 63s. net.)

THE volume under review gives a further large instalment of Professor Cullis's large work. The printing of volume 3 was suspended for several years during the completion of some investigations which have necessitated the division of it into two parts and the carrying forward of some of the matter designed for it into a later volume.

The present book is a mine of information, and, like the previous volumes, should be of the greatest value to those working on the subjects with which it deals.

*An Introduction to the Theory of Infinite Series.* By T. J. I'A. BROMWICH. Second Edition revised with the assistance of T. M. MACROBERT. (London: Macmillan & Co., 1926. 30s. net.)

IT is a great satisfaction to welcome the second edition of Dr. Bromwich's 'Infinite Series.' The first edition was issued in 1908, and during the last few years copies have been very difficult to obtain. In the new edition Dr. MacRobert has rendered valuable assistance to the author.

There are various minor changes in the new edition. A discussion of the solution of linear differential equations of the second order has been added; also an account of certain elliptic function formulæ. In the chapters concerned with asymptotic expansions an exposition of the asymptotic expansions of Bessel functions is now included.

To the appendices there is added an account of Napier's invention of logarithms.

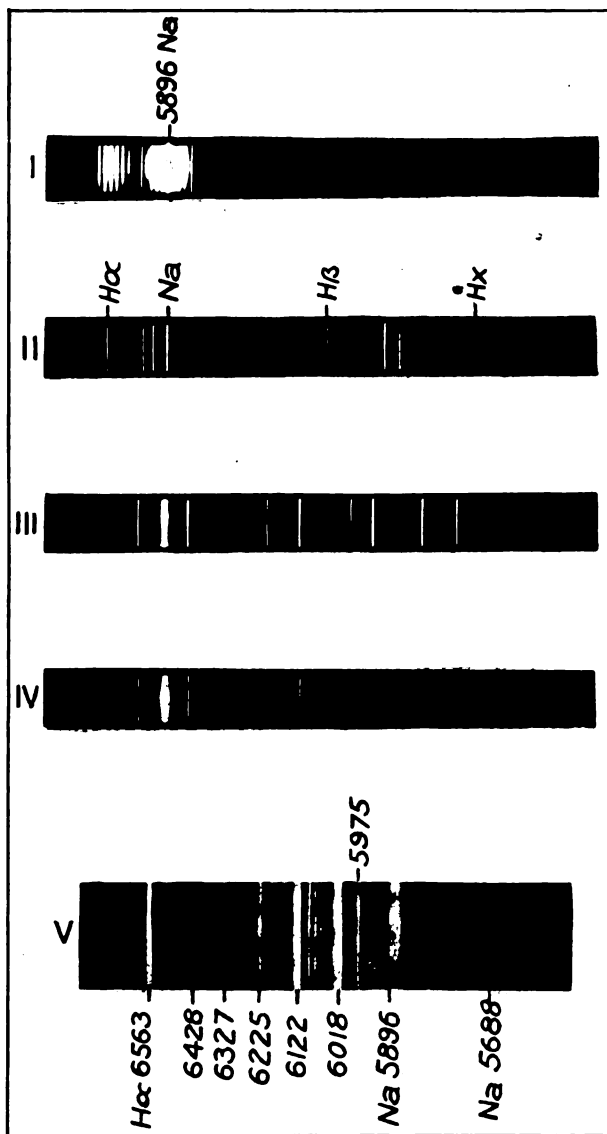
*Principles of Geometry.* Vol. IV. *Higher Geometry.* By H. F. BAKER. (Cambridge University Press, 1925. 15s. net.)

THIS volume of Professor Baker's 'Geometry' is concerned with showing the utility of the consideration of higher space, especially of four and five dimensions. It is a remarkable fact that it is possible to comprehend under one simple point of view the introduction to nearly all the surfaces ordinarily studied in the geometry of three dimensions, as well as the usual line geometry. The present volume develops this point of view.

The student of geometry will give the present volume the same warm welcome which has been extended to the volumes previously issued. He will be specially grateful for the excellent index.

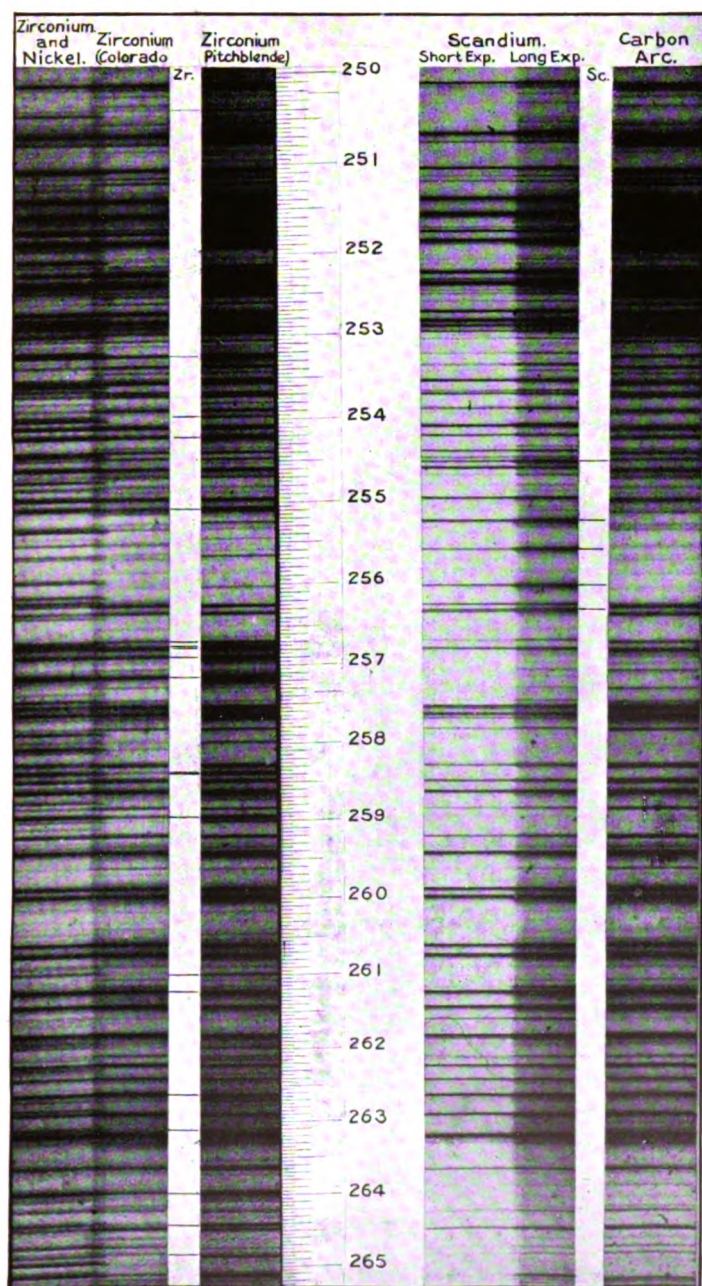
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[The Editors do not hold themselves responsible for the views expressed by their correspondents.]



SPECTRA OF THE SODIUM ARC IN VACUO.







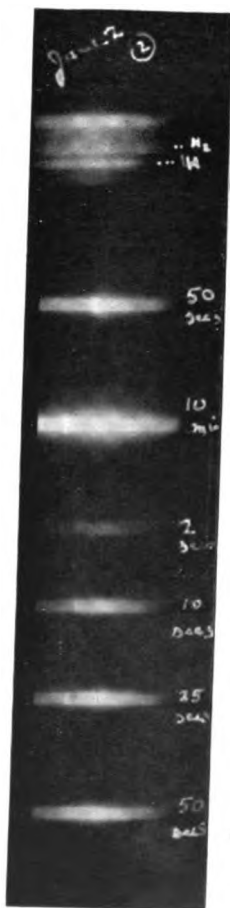
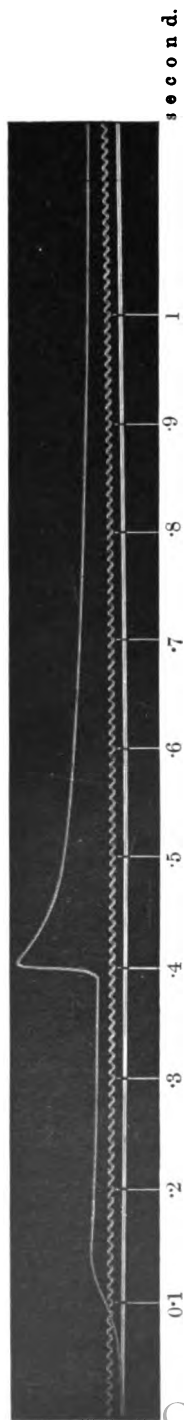




FIG. 3.



FIG. 4.







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[SEVENTH SERIES.]

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JUNE 1926.

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CIX. *The  $\beta$ -Rays associated with Scattered X-Rays.* By J. M. NUTTALL, M.Sc., Senior Lecturer in Physics, University of Manchester, and E. J. WILLIAMS, M.Sc., Fellow of the University of Wales \*.

[Plates XIX.-XX.]

I. INTRODUCTION.

C. T. R. WILSON† and others‡, using the cloud method, have shown that the  $\beta$ -ray tracks produced in air by relatively hard X-rays are of two distinct types, distinguished chiefly by their relative lengths. The types are: (a) long tracks due to electrons ejected with initial kinetic energy comparable to a quantum of the incident radiation: these tracks are due to the photoelectrons ejected from atoms which have each absorbed one quantum of the primary X-rays; (b) tracks of very short range which have been associated with the scattering of the incident X-rays, A. H. Compton§ having shown that such tracks were a necessary consequence of his quantum theory of scattering. According to this theory, a single electron may scatter a single quantum of X-rays, the electron as the result of the encounter acquiring momentum equal to the vector-difference

\* Communicated by Prof. W. L. Bragg, F.R.S.

† C. T. R. Wilson, Proc. Roy. Soc. A, civ. p. 1 (1923).

‡ Bothe, *Zeit. f. Phys.* xvi. p. 329 (1923); Compton and Simon, *Phys. Rev.* xxv. p. 306 (1925).

§ Compton, Bull. Nat. Res. Coun. xx. p. 19 (1922).

between that of the quantum before and after scattering. If the energy thus acquired by the electron is sufficiently large, it will leave the atom to which it is bound and give rise to a short  $\beta$ -ray. These are the rays which on the quantum theory of scattering are identified with the above-mentioned short tracks. The object of the work commenced in the experiments to be described in this paper, is to examine the number, length, and orientation of the *short* tracks produced in different gases by homogeneous X-rays of various known wave-lengths, and to compare the results with the requirements of the quantum-scattering theory of their origin. The present paper \* will deal mainly with the number of short tracks in the gases oxygen, nitrogen, argon, and hydrogen, for X-rays of a few different wave-lengths. It is hoped later to extend the results to X-rays of shorter wave-length and it will then be possible to discuss the question of the length and orientation of the short tracks. During the progress of the work Compton and Simon† have published the results of a series of experiments on the  $\beta$ -ray tracks produced in air by approximately homogeneous X-rays, using the Wilson method. The results of their experiments bear out the quantum scattering theory of the origin of the short tracks, though they can hardly be considered as a very adequate test of the theory for the following reasons:—(1) The total number of tracks examined is small and it is obviously desirable to examine a large number, since the relation to be tested is a statistical one. (2) According to the theory the relative number of the two types of tracks varies approximately as  $1/\lambda^3$ , where  $\lambda$  is the wave-length of the incident X-rays. It is therefore of the highest importance that the wave-length of the X-rays should be accurately known, whereas in Compton and Simon's experiments the rays were only approximately homogeneous. In the present experiments the probable errors arising from the two above-mentioned causes have been very considerably reduced. In the first place about 4000 tracks have been counted involving the examination of more than 300 pairs of stereoscopic photographs, and secondly, we have used the crystal reflexion method to obtain a very homogeneous beam of X-rays of accurately known wave-length.

\* An account of some of the observations given in this paper has already been published by the authors in the *Memoirs of the Manchester Literary and Philosophical Society*, No. 1, vol. lxx., 13th Oct. 1925.

† Compton and Simon, *Phys. Rev.* xxv. p. 306 (1925).

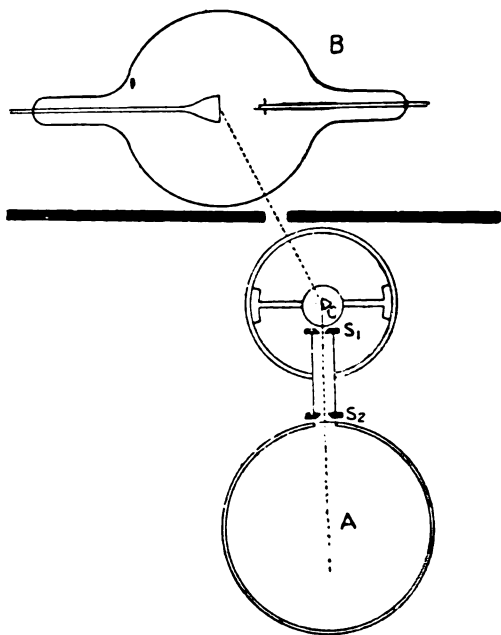
## II. EXPERIMENTAL ARRANGEMENT.

The cloud-expansion apparatus used in the present investigation is of the well-known Wilson pattern and needs no further description. It is adapted so that different gases can be introduced into the cloud-chamber. The source of X-rays is a Coolidge tube excited by the discharge from Leyden jars maintained at a high potential from a Wimhurst machine. A second battery of Leyden jars, discharged through a mercury spark-gap, provides the illuminating "flash." The intervals between the expansion of the gas in the cloud-chamber, the passage of the X-rays, and the illuminating flash are carefully "timed" by trial until clear photographs of the  $\beta$ -ray tracks are obtained. In all cases stereoscopic pairs of photographs are taken, the camera lenses being Beck Isostigmars of maximum aperture f. 5.8. Imperial Eclipse plates have been found satisfactory.

In a quantitative study of the  $\beta$ -rays produced by a beam of X-rays it is of the greatest importance, as previously pointed out, that the rays used should be as nearly as possible homogeneous and of known wave-length. This has been done throughout the present series of experiments by using the X-rays reflected from a crystal at a known "setting." The experimental arrangement for obtaining a beam of homogeneous X-rays is shown in fig. 1. The slits  $S_1$ ,  $S_2$ , which limit the beam that can enter the cloud-chamber A (through the mica window W) are fixed. The crystal C can be rotated, and for any definite setting X-rays of wave-length corresponding to that setting only, can enter the chamber A. The position of the Coolidge tube B (which is enclosed in a lead box) can be adjusted for any setting of the crystal C till a reflexion is obtained. The "homogeneity" of the beam obtained will depend on the width of the slits and their distance apart and to a certain extent on the nature of the crystal used. In sifting out some particular wave-length from the general radiation from the Coolidge tube, there is one other point to remember. For any setting  $\theta$  of the crystal with respect to the fixed slits all wave-lengths (provided they are present in the radiation from the tube) which satisfy the relation  $n\lambda = 2d \sin \theta$  may be reflected into the cloud-chamber. Thus we may get wave-lengths  $\lambda$ ,  $\lambda/2$ ,  $\lambda/3$  ... corresponding to 1st, 2nd, 3rd order reflexions, the relative intensities of the different orders depending on the crystal used. In the earlier experiments in this work a rocksalt crystal and moderately wide slits were used, giving the wave-length to approximately  $0.5 \text{ \AA}$ .

Using the general radiation from a tungsten Coolidge tube and the rocksalt crystal, series of photographs were taken of the  $\beta$ -ray tracks produced in air by X-rays of wave-lengths  $\cdot 57 \text{ \AA}$  and  $\cdot 35 \text{ \AA}$ . (The results are tabulated later.) The rocksalt crystal was then replaced by a *diamond* in order to eliminate the possibility of a 2nd order reflexion. Although the intensity of the 2nd order reflexion in the case of rocksalt is only about one-fifth that of the first order, a few

Fig. 1.



photographs were obtained in which there were observed  $\beta$ -ray tracks produced by X-rays of wave-length corresponding to the higher order reflexion. In the case of the diamond there is practically no 2nd order reflexion from the  $[1.1.1]$  face, and the excitation of rays corresponding to higher orders is prevented by control of the potential applied to the tube. In general it is undesirable to use this latter control to prevent the 2nd order reflexion, as the lowering of the potential to the necessary value interferes too much with the output of X-rays. In the final arrangement used, the slits were  $1/5$  mm. wide and 10 cm. apart, and

the wave-length of the beam of X-rays entering the cloud-chamber was known to  $\cdot 01 \text{ \AA}$ . With this arrangement about 250 stereoscopic pairs of photographs have been taken, using the  $K\alpha$  ( $\cdot 614 \text{ \AA}$ ) and  $K\beta$  ( $\cdot 545 \text{ \AA}$ ) radiations from a rhodium Coolidge tube and the  $K\alpha$  ( $\cdot 709 \text{ \AA}$ ) radiation from a molybdenum tube.

The tracks produced by the above rays in the following gases have been examined:—oxygen, nitrogen, argon, hydrogen, and a mixture of hydrogen with a known small percentage of argon. The gases used were supplied commercially and were not specially purified. In the cases of the oxygen and nitrogen this is relatively unimportant, but in the case of the *argon* allowance had to be made for the relatively large proportion of nitrogen (about 15 per cent.) which it contained. There was no evidence of an appreciable amount of impurity in the hydrogen.

### III. EXAMINATION OF PHOTOGRAPHS.

A few typical photographs have been reproduced in Plates XIX. and XX. and show the nature of the  $\beta$ -ray tracks in different gases and for different wave-lengths of X-rays. It is seen that the tracks in all the photographs can be divided into the two classes previously mentioned, viz. one class consisting of short tracks and the other of tracks with a length of the order of a cm. Though the short tracks only appear as "spots" on the plates, it is possible by simple tests to ascertain their genuine nature and thus avoid confusing them with spots which sometimes appear on the plates but which are not photographs of  $\beta$ -ray tracks.

### IV. DISTRIBUTION OF SHORT TRACKS WITH RESPECT TO THE ORIGINS OF THE LONG TRACKS.

In an account of the nature of the  $\beta$ -rays produced by X-rays, C. T. R. Wilson\* describes paired tracks in which one of the pairs is a long track and the other a short track, the origins of the tracks being slightly separated. This is stated to occur only with rays of wave-length less than about  $\cdot 5 \text{ \AA}$ . Though this excludes most of the present experiments, observations in certain cases have been made on the distribution of the short tracks in order to see if there is any tendency for them to occur near the origins

\* C. T. R. Wilson, Proc. Roy. Soc. A, civ. p. 1 (1923).



of long tracks. A further reason for making these observations is to test the accuracy of the procedure adopted in counting the total number of short tracks on a plate. In the case of a spot which is within a fraction of a mm. of the origin of a long track, it is very difficult to ascertain with certainty whether it is a part of the long track or a separate short track. In the procedure we have adopted the number,  $N'_R$ , of short tracks *excluding* those within a mm. of the origin of long tracks is first counted. The number,  $N_{R1}$ , of short tracks excluded is then calculated on the assumption that the short tracks are randomly distributed. The sum,  $N'_R + N_{R1}$ , then gives the total number  $N_R$ , of short tracks on the plate. A spot at a distance greater than a mm. from the origin of a long track is not part of that track and is certainly a photograph of a separate short  $\beta$ -ray track. There is therefore little or no uncertainty concerning these, and the distribution of short tracks on the plates has been tested by counting the number,  $N_{R1,2}$ , of short tracks at distances between 1 and 2 mm. from the origins of long ones, as well as counting the total number of short tracks outside a mm. range of the long ones. The beam of X-rays in the cases investigated was in the form of a thin sheet approximately normal to the axis of the camera, so that the distribution of points in the beam reduces to that of points on a plane. The theoretical relation of  $N_{R1,2}$  to  $N'_R$  on the assumption that the short tracks are randomly distributed will now be considered.

Let  $A$  = area in sq. mm. of the beam of X-rays on the plate.

$N_P$  = number of long tracks.

$N_R$  = total number of short tracks.

$N'_R$  = number of short tracks, at distances on the plate greater than 1 mm. from origins of long tracks.

$N_{Ra}$  = number of short tracks within a distance " $a$ " mm. of origins of long tracks.

Then total area of circles of radius  $a$  drawn round origins of long tracks  $= N_P \cdot \pi a^2$ .

Average number of short tracks per mm.<sup>2</sup>  $= N_R/A$ .

Assuming a random distribution of short tracks,

$$N_{Ra} = \left[ \frac{N_R}{A} \right] \times N_P \cdot \pi a^2, \quad \dots \dots (1)$$

and for a series of photographs,

$$N_{Ra} = \frac{\pi a^2}{A} \cdot \Sigma N_R \cdot N_P \quad \dots \dots (2)$$

The possibility of two circles overlapping one another or of a circle extending outside the boundary of the beam has been neglected. To allow for the former the expression for

$N_{Ra}$  must be multiplied by the factor  $\left[1 - \frac{(N_P - 1)\pi a^2}{2A}\right]$

and to allow for the latter by the factor  $[1 - 4a/3\pi t]$ , where  $t$  is the width in mm. of the approximately rectangular beam. It can readily be shown that the corrected expression for  $N_{Ra}$  (making certain approximations) is given by

$$N_{Ra} = \frac{\pi a^2}{A} \left\{ 1 - \frac{4a}{3\pi t} \right\} \cdot \Sigma N'_R \cdot N_P \cdot \left\{ 1 - \frac{\pi \cdot N_P}{2A} \cdot (a^2 - 2) \right\} \quad \dots (3)$$

In the experiments made with diamond as the reflecting crystal,

$$A = 760 \text{ mm.}^2, \quad t = 8.5 \text{ mm.}$$

On substituting these values in (4) we find that

$$N_{R1.2} = .0040 \{ \Sigma N'_R \cdot N_P + \Sigma N'^2_R / 480 \} \quad \dots (4)$$

$$N_{R1.2} = .015 \{ \Sigma N'_R \cdot N_P - \Sigma N'^2_R / 240 \} \quad \dots (5)$$

The results of the examination of a number of plates are given in Table I.

TABLE I.

Gas.	Wave-length in Å.	$N_{R1.2}$		$N'_R$ (obs.).	$N_{R1}$ (calc.).	$N_R = N'_R + N_{R1}$
		Calculated.	Observed.			
Oxygen .....	.709	5	3	24	2	26
" .....	.614	30	37	114	15	129
" .....	.545	11	10	105	4	109
Nitrogen <i>a</i> ...	.614	11	19	89	4	93
" <i>b</i> ...	.614	27	33	117	13	130
" .....	.545	9	5	106	3	109
Total		93	107			

The first and second columns give the gas traversed and the wave-length of the X-rays. The *calculated* numbers  $N_{R1.2}$  of tracks at a distance between 1 mm. and 2 mm. from the origins of long tracks are given in column (3) and in column (4) the numbers actually observed are given. The agreement between the calculated and observed values of  $N_{R1.2}$  is seen to be fairly good, the observed values in some

cases being less than the calculated probable values and in others greater. Since the calculated values are based on the assumption that the short tracks are randomly distributed, the agreement with the observed values shows that the assumption of such a distribution is justified, at least in the cases of short tracks produced at distances greater than 1 mm. from the origins of long tracks in the gases oxygen and nitrogen, at pressures of about 60 cm., and for X-rays of wave-lengths  $\cdot 545 \text{ \AA}$ ,  $\cdot 614 \text{ \AA}$ , and  $\cdot 709 \text{ \AA}$  respectively. If there is any tendency for short tracks to occur near the origins of long ones for X-rays of these wave-lengths (as pointed out by Wilson for slightly harder X-rays), then they must be produced within a mm. of the origins of the long tracks.

In the sixth column of Table I. are given the calculated values of  $N_{R1}$  which, when added to the values of  $N'_R$  of column (5), give the total number of short tracks  $N_R^*$ . These are given in the last column of the Table and are the values used in the later discussion of the number of short tracks.

#### V. THE RATIO OF THE NUMBER OF SHORT TRACKS TO THE NUMBER OF LONG TRACKS.

Before giving the results which have been obtained in connexion with the relative number of the short and long tracks, the theoretical values of this ratio on the basis of Compton's quantum scattering theory of the origin of the short tracks will first be considered.

##### *Calculation of $N_R/N_P$ on Compton's Theory.*

Compton and Hubbard † showed that since on the quantum theory each scattered quantum of X-rays is associated with a recoil electron, and each absorbed quantum with a photo-electron, then the ratio of the number of recoil electrons to the number of photo-electrons, is equal to the ratio of the number of scattered quanta to the number of absorbed quanta, *i. e.* is equal to the ratio of the scattering coefficient,

\* Clearly this statement is incorrect if there are more *short* tracks within a mm. range of the long tracks than is consistent with a random distribution. However, such additional tracks would represent a different phenomenon from that which operates in the production of the class of short tracks which are randomly distributed, and therefore such tracks do not concern us here.

† Compton and Hubbard, *Phys. Rev.* **xxiii.** p. 448 (1924).

$\sigma$ , to the absorption coefficient,  $\tau$ . In this calculation of  $N_R/N_P$  the possibility that a scattered quantum may not give sufficient energy to the scattering electron to enable the latter to leave the atom is neglected. To allow for this possibility it is necessary to multiply  $\sigma/\tau$  by a factor  $f$ , where  $f$  represents the fraction of scattered quanta which give the required energy to the scattering electron. The ratio  $N_R/N_P$  is then given by

$$\frac{N_R}{N_P} = f \cdot \frac{\sigma}{\tau}.$$

$f$  depends on the wave-length of the X-rays and on the binding energies of the electrons, and its value will be calculated in an Appendix at the end of the paper \*. In order, therefore, to determine the theoretical values of  $N_R/N_P$ , we require to know the values of  $\sigma/\tau$ , and for this purpose the results obtained by C. W. Hewlett † have been assumed. Hewlett has determined the total mass absorption coefficients of a number of light elements for homogeneous X-rays varying in wave-length from  $0.1 \text{ \AA}$  to  $1.0 \text{ \AA}$ . According to his results the total mass absorption coefficient  $\mu/\rho$  of an element of atomic number  $N$  and for radiation of wave-length  $\lambda$  is given by

$$\frac{\mu}{\rho} = KN^3\lambda^3 + \frac{\sigma}{\rho},$$

where  $\sigma/\rho$  is the mass scattering coefficient, the term  $KN^3\lambda^3$  representing the true mass absorption coefficient  $\tau/\rho$ . For oxygen, Hewlett's value of  $K$  is  $5.71 \times 10^{-3}$  and  $\sigma/\rho$  is  $0.165$ . There is no evidence in Hewlett's results to show that  $K$  is different for nitrogen though he gives it a slightly different value, and for nitrogen the same values of  $K$  and  $\sigma/\rho$  have been used as in the case of oxygen. The values of  $K$  and  $\sigma/\rho$  assumed for argon are  $5.87 \times 10^{-3}$  and  $0.177$  respectively, being intermediate between the values given by Hewlett ‡ for aluminium and iron. From these values,  $\sigma/\tau$  for any of these gases and any wave-length can be obtained. In some of the experiments mixtures of gases have been used, and for such mixtures the theoretical value of  $N_R/N_P$  is given by

$$\frac{N_R}{N_P} = \frac{\sum f'n\sigma}{\sum n\tau},$$

where  $n$  denotes the relative number of atoms of which the

\* See Table V. for values of " $f$ ."

† C. W. Hewlett, Phys. Rev. xvii. p. 284 (1921).

‡ Hewlett's values of  $K$  and  $\sigma/\rho$  for aluminium are  $5.71 \times 10^{-3}$  and  $0.173$ , and for iron  $6.03 \times 10^{-3}$  and  $0.180$ .

absorption and scattering coefficients are  $\tau$  and  $\sigma$  respectively. This completes the data necessary for the evaluation of the theoretical values of  $N_R/N_P$ , and the results obtained and shown in Table II. will now be considered.

TABLE II.

Gas.	Wave-length in Å.	No. of stereoscopic pairs of plates examined.	$N_P$ .	$N_R$ .	$\frac{N_R}{N_P}$ .	$\frac{\sigma}{\tau}$ .	$f$ .	Theoretical value of $\frac{N_R}{N_P}$ $= \sigma/\tau \times f$ .
Oxygen.....	709	22	205	26	127	174	816	142
Oxygen.....	614	34	608	129	212	268	843	226
Oxygen.....	545	50	358	109	305	383	866	332
Nitrogen ...	614	46	722	223	309	400	850	340
Nitrogen ...	545	34	202	109	540	572	876	501
† Argon .....	614	10	209	7	033	030	69*	021
† Argon .....	545	9	139	4	029	043	73*	031
Air .....	57	37	454	153	337	372	865*	322
Air .....	35	11	83	139	167	157	94*	148

† Argon contained 15 per cent. of nitrogen.

\*  $f$  in these cases =  $\frac{\sum f/n\sigma}{\sum n\sigma}$ .

The first two columns in Table II. give the gas in the cloud-chamber and the wave-length of the radiation. In the fourth column are given the numbers,  $N_P$ , of long or photo-electron tracks produced, and in the fifth column the numbers,  $N_R$ , of short tracks, whilst the third column gives the numbers of stereoscopic pairs of photographs examined in each case. The ratios of  $N_R$  to  $N_P$  are given in column (6). The theoretical values of this ratio, calculated from the values of  $\sigma/\tau$  given in column (7) and the values of " $f$ " in column (8), are given in the last column. It will be seen from the Table that the difference between the observed and theoretical values of  $N_R/N_P$  (except in the case of argon, where the probability error is large as there are very few short tracks) is in no case greater than 13 per cent., the average difference being 9 per cent. These differences are within the experimental errors involved in the determination of  $N_R/N_P$ ,  $\sigma$ , and  $\tau$ . The error in the observed value of  $N_R/N_P$  arises from the fact that only a limited number of tracks are counted, and it has been computed that the average error in the various cases, due to this, is about 7 per cent. ‡ The values of  $\sigma$  and  $\tau$  for

‡ If  $n$  is the average number of tracks produced under given conditions, then the probability that  $r$  tracks be produced under these conditions is  $n^r \times e^{-n}/r!$ —this formula has been used in estimating the average error.

oxygen are, according to Hewlett, probably correct to 1 or 2 per cent. For nitrogen the possible error is more and may be as much as 7 or 8 per cent. The error involved in " $f$ " is probably less than 1 per cent., as  $f$  only varies slowly with the quantities involved in its determination. It may be concluded from these estimates of the errors that the average difference of 9 per cent. between the calculated and observed values of  $N_R/N_P$  can be accounted for by experimental error. We thus see that the numbers of short tracks produced in the various cases included in Table II. agree within the error of experiment, with the numbers required by Compton's theory.

*The Number of Short Tracks produced in Hydrogen.*

The true absorption of X-rays by hydrogen is so small that, on Compton's theory, there should be a predominance of short tracks even when the ionizing rays are comparatively soft. Observations made on the tracks produced in hydrogen should therefore provide an additional interesting test of the theory. The absorption in hydrogen is, as already stated, very small and has in fact never been truly measured. In the Wilson method of observing the  $\beta$ -rays, water-vapour is essentially present in the cloud-chamber and the absorption due to this is large compared with the true absorption in hydrogen, and the latter can be neglected\*. The amount of water-vapour present at ordinary temperatures is about 2 per cent., and according to the theory the ratio  $N_R/N_P$  should be about ten times greater than in the case of pure oxygen or nitrogen. Two series of photographs of the  $\beta$ -ray tracks produced in hydrogen by X-rays of wave-length  $0.614 \text{ \AA}$  have been taken, the two series corresponding to two different temperatures and therefore different percentages of oxygen atoms. The results of the two series of photographs are given in Table III.

Column (1) gives the relative numbers of hydrogen and oxygen atoms in the cloud-chamber, and columns (5) and (6) the observed and theoretical values of  $N_R/N_P$ . The agreement is satisfactory, the smaller value of the observed ratio being expected if there is any impurity in the hydrogen, as this would obviously increase the observed number of photo-electron tracks  $N_P$ . (This is shown by giving in the

\* The effect of the water vapour on the theoretical value of the ratio  $N_R/N_P$  in the cases discussed in Table II. is quite inappreciable.

last column of the Table the theoretical number of photo-electron tracks expected in each case, which is seen to be less than the number observed). A further series of photographs of the tracks produced by X-rays of wavelength  $614 \text{ \AA}$  were taken when a small percentage of argon was introduced into the hydrogen filled cloud-chamber.

TABLE III.

Proportion of hydrogen and oxygen atoms in cloud-chamber.	$\lambda$ in $\text{\AA}$ .	$N_P$	$N_R$	$\frac{N_R}{N_P}$	Theoretical value of $\frac{N_R}{N_P} = f\sigma/\tau$ .	Theoretical value of $N_P$ calculated from columns (4) and (6).
Hydrogen : Oxygen = 200 : 2.3 ...	614	11	28	2.5	2.9	10
Hydrogen : Oxygen = 200 : 1.47 ...	614	21	73	3.5	4.4	16

The argon has the effect of increasing the number of photo-electron tracks and the value of  $N_R/N_P$  should be reduced. The photographs are interesting from another point of view, as they show the "tertiary"  $\beta$ -ray tracks produced by the K radiation of argon, as previously pointed out by Auger\*. The absorption of a quantum of the incident radiation by an argon atom is accompanied by the ejection of a photo-electron (secondary  $\beta$ -ray) from that atom and the emission of the fluorescent K radiation of argon. The latter radiation subsequently ejects an outer electron from the same atom, and this electron has sufficient energy (about 4000 volts) to produce in the hydrogen atmosphere of the cloud-chamber a short  $\beta$ -ray track—the tertiary  $\beta$ -ray. In photograph 10 of Plate XX. these short tertiary tracks can be seen quite clearly starting from the same origin as the long photo-electron tracks.

The results showing the values of  $N_R$ ,  $N_P$ , etc. for two different percentages of argon are given in Table IV. The first column gives the relative number of atoms of hydrogen, oxygen, argon, and nitrogen in the cloud-chamber, whilst columns (5) and (6) give the observed and theoretical values of  $N_R/N_P$ . The agreement is again seen to be satisfactory. The last column shows the expected number of recoil tracks calculated from the numbers in columns (3) and (6).

\* Auger, *Journal de Physique*, vi. No. 6, p. 205 (1925).

The results discussed in Tables II., III., IV., which cover a range of wave-lengths of the incident X-rays from  $\cdot 35 \text{ \AA}$  to  $\cdot 709 \text{ \AA}$ , and the gases oxygen, nitrogen, argon, and hydrogen, consistently show a remarkably good agreement between the observed values of  $N_R/N_P$  and the values which would be expected on the quantum theory of scattering, and constitute almost conclusive evidence in favour of that theory. It should be emphasized that the theoretical values

TABLE IV.

Composition of gas in cloud-chamber.	$\lambda$ in $\text{\AA}$ .	$N_P$ .	$N_R$ .	$\frac{N_R}{N_P}$ .	Theoretical $N_R/N_P$ .	Theoretical values of $N_R$ .
H : O : A : N = 197.4 : 1.5 : 1.1 : 4	$\cdot 614$	62	15	$\cdot 24$	$\cdot 19$	12
H : O : A : N = 198.6 : 1.5 : .53 : 3	$\cdot 614$	71	28	$\cdot 39$	$\cdot 34$	24

of the ratio are based on the assumption that *all* the scattered radiation obeys the quantum theory of scattering. The spectrum of the scattered X-radiation has been shown to consist of a "modified" line and an "unmodified" one, the latter having the same wave-length as the primary radiation. The results of the present experiments show that either the unmodified radiation is produced according to the quantum theory or is present in the cases investigated in these experiments to an extent less than the experimental error, *i. e.* less than about 10 per cent. of the total scattered radiation.

#### *Relation of the Short Tracks to the J Phenomenon.*

According to C. G. Barkla\* the Compton effect is a manifestation of the more general J phenomenon. One remarkable property of the J phenomenon is that quite frequently it does not occur at all though the conditions may be apparently unaltered from those under which it has previously been observed. This is, however, not a characteristic of the short  $\beta$ -rays observed in the present experiments. These rays are produced in all cases in which the strength of the primary beam is such as to provide a reasonable expectation of a short  $\beta$ -ray. Thus one of the main properties of the J phenomenon is *not* characteristic of the phenomenon of the production of short  $\beta$ -rays by X-rays.

\* Phil. Mag. ser. 6, vol. 1. p. 1133, Nov. 1925.



Neither has this property been observed in investigations of the change of wave-length due to scattering, but Barkla attributes this fact to the "duration" of the experiments. The non-manifestation of the property under the conditions of the present experiments cannot be similarly explained, since each experiment only involves a single instantaneous discharge through the X-ray tube and is therefore of the shortest possible duration. It should, however, be noted that each of the present experiments involves all directions of scattering.

*Calculation of " $f$ " \* †.*

The electron in scattering a quantum of X-rays acquires momentum equal to the vector difference between the momentum of the quantum before and after scattering. The energy gained by the electron is taken from the quantum which after scattering is characteristic of radiation of longer wave-length. The scheme is represented in figs. 2 *a* and 2 *b*.

Let  $\lambda$  = wave-length of incident X-radiation. Assume fraction  $p$  of the electrons in the scattering material possess orbital kinetic energy  $B^2$  and ionization potential  $V$ . Consider quanta scattered through angles between  $\theta$  and  $\theta + d\theta$  by electrons belonging to this class, and let  $f_1$  be the fraction of these which give recoil tracks. Consider an encounter in which the velocity of the electron before scattering makes an angle  $\phi$  with the momentum communicated to it by the quantum (fig. 2 *b*).

We have

$$M_1^2 = \left(\frac{h}{\lambda}\right)^2 + \left(\frac{h}{\lambda + d\lambda}\right)^2 - 2 \cdot \frac{h}{\lambda} \cdot \frac{h}{\lambda + d\lambda} \cdot \cos \theta. \quad (1)$$

\* Jauncey (Phys. Rev. xxv. p. 314, 1925 and xxv. p. 723, 1925) has made calculations on the relative intensities of the modified and unmodified scattered radiations: in those cases it is only necessary to consider radiation scattered in one direction, whilst in the problem under consideration it is necessary to take into account the total scattered radiation.

† This calculation of " $f$ " was first given by the authors in a paper read before the Manchester Lit. and Phil. Soc. in October 1925. In the Physical Review for the same month Jauncey also pointed out the necessity for the " $f$ " correction. Jauncey assumed that a recoil electron, after escaping from the parent atom, must have an amount of energy at least equal to about 650 volts, before it can be detected by the cloud method. He gives corrected values of  $N_R/N_P$  for air in the cases investigated in Compton and Simon's experiments (*loc. cit.*). The cloud method is, however, capable of showing individual ions, and accordingly in the present work it is assumed that the ejection of an electron from an atom (no matter how small the surplus energy) will be recorded.

The energy gained by the electron is  $(M^2 - M_2^2)/2m$ , where  $m$  is the mass of the electron, and if it is able to leave the atom, we have

$$\frac{1}{2m}(M^2 - M_2^2) > V. \quad \dots \quad (2)$$

Fig. 2 a.

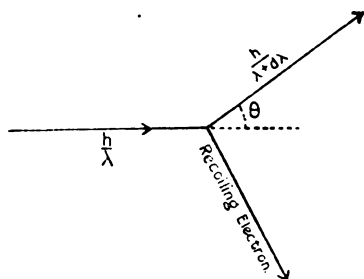
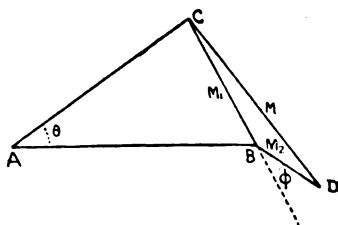


Fig. 2 b.



AB	represents the momentum	$hc/\lambda$	of the incident quantum.
AC	"	$hc/\lambda + d\lambda$	of the scattered quantum.
CB	"	$M_1$	communicated to the electron.
BD	"	$M_2$	of the electron <i>before</i> scattering.
CD	"	$M$	of the electron <i>after</i> scattering.

(ABC and CBD are not necessarily in the same plane.)

There are three cases to consider :

- (a) The inequality (2) may be satisfied by all values of  $\phi$  between 0 and  $\pi$ , in which case  $f=1$ .
- (b) It may be satisfied by no values of  $\phi$ , in which case  $f=0$ .
- (c) It may be satisfied by some but not all values of  $\phi$ .

In case (c) there exists a value,  $\phi_c$ , of  $\phi$  which is such that (2) is satisfied by all values of  $\phi$  less than  $\phi_c$ . When  $\phi = \phi_c$ , the energy communicated to the electron is just sufficient to eject it from the atom, so that  $\phi_c$  is the value of  $\phi$  which satisfies

$$\frac{1}{2m}(M^2 - M_2^2) = V. \quad \dots \quad (3)$$

From fig. 2 b,

$$\cos \phi = \frac{(M^2 - M_2^2 - M_1^2)}{2M_1M_2}.$$

So that from (3),

$$\cos \phi_c = \frac{2mV - M_1^2}{2M_1M_2}. \quad \dots \quad (4)$$

When  $\phi = \phi_c$ , the energy,  $h/\lambda - h/\lambda + d\lambda$ , lost by the quantum is  $V$ , and as  $V$  for light elements is small compared with  $h/\lambda$ , equation (1) becomes

$$M_1^2 = 2m\psi^2 \sin^2 \theta/2,$$

where

$$\psi = \sqrt{\frac{2}{m} \cdot \frac{h}{\lambda} \left[ 1 - \frac{V\lambda}{2hc} \right]}.$$

Substituting this value of  $M_1$  in (4) and replacing  $M_2$  by  $B\sqrt{2}m$ , we have

$$\cos \phi_c = \frac{1}{2} \cdot \frac{V}{\psi B \sin \theta/2} - \frac{1}{2} \frac{\psi}{B} \sin \frac{\theta}{2}.$$

Since the direction of scattering is independent of the motion of the scattering electron (the latter being for light elements almost negligible compared with the velocity of light) the value of the fraction  $f_2$  of electrons for which  $\phi < \phi_c$  is given by

$$f_2 = \frac{1 - \cos \phi_c}{2} = \frac{1}{2} + \frac{1}{4} \frac{\psi}{B} \sin \frac{\theta}{2} - \frac{1}{4} \frac{V}{\psi B \sin \theta/2}. \quad (5)^*$$

There will in general be two values  $\theta_1$  and  $\theta_2$  of  $\theta$ , such that the values of  $\theta$  less than  $\theta_1$  belong to case (b), the values of  $\theta$  between  $\theta_1$  and  $\theta_2$  to case (c), and the values of  $\theta$  between  $\theta_2$  and  $\pi$  to case (a). Hence in the region defined by  $0 < \theta < \theta_1$ ,  $f = 0$ , in the region defined by  $\theta_1 < \theta < \theta_2$ ,  $f$  is given by (5), and in the region defined by  $\theta_2 < \theta < \pi$ ,  $f$  is unity. The value of  $\theta_1$  is given by (5) when  $f_2$  is put equal to zero. The value thus obtained is given by

$$\sin \frac{\theta_1}{2} = \frac{\sqrt{B^2 + V} - B}{\psi} = \alpha, \text{ say.} \quad (6)$$

If there are no values of  $\theta$  which make  $f_2$  unity then  $\theta_2 = \pi$ , and this is the case if  $\psi^2 - 2\psi B - V < 0$ .

If  $\psi^2 - 2\psi B - V \geq 0$ ,  $\theta_2$  is given by

$$\sin \frac{\theta_2}{2} = \frac{\sqrt{B^2 + V} + B}{\psi} = \beta, \text{ say.} \quad (7)$$

In the case of light elements the intensity of scattering in a direction  $\theta$  varies approximately as  $(1 + \cos^2 \theta)$ , whence the fraction of scattered quanta, scattered between  $\theta$  and  $\theta + d\theta$ , is  $\frac{2}{3} \sin \theta (1 + \cos^2 \theta) d\theta$ .

\* On Jauncey's theory of the modified radiation,  $f_2$  represents the fraction of the radiation which is modified, and Jauncey derived an expression for it similar to (5).

The fraction of these which produce recoil tracks is  $f_2$ , so that the fraction  $f_1$  of quanta scattered in all directions which give rise to recoil tracks is given by

$$f_1 = \int_0^\pi \frac{2}{3} \sin \theta (1 + \cos^2 \theta) \cdot f_2 d\theta \\ = \int_{\theta_1}^{\theta_2} \frac{2}{3} \sin \theta (1 + \cos^2 \theta) \left\{ \frac{1}{2} + \frac{\psi}{4B} \sin \frac{\theta}{2} - \frac{V}{4\psi B \sin \theta/2} \right\} d\theta \\ + \int_{\theta_2}^\pi \frac{2}{3} \sin \theta (1 + \cos^2 \theta) d\theta,$$

where  $\theta_1$  is given by (6),

and  $\theta_2 = \pi$  if  $\psi^2 - 2\psi B - V < 0$ ,

and is given by (7) if  $\psi^2 - 2\psi B - V \geq 0$ .

This gives on integration

$$f_1 = \left[ \frac{3}{4} \left\{ (\delta_2 - \delta_4 - \frac{2}{3}\delta_6) + \frac{\psi}{B} \left( \frac{1}{3}\delta_2 - \frac{2}{3}\delta_6 + \frac{2}{3}\delta_7 \right) \right. \right. \\ \left. \left. - \frac{V}{\psi B} (\delta_1 - \frac{2}{3}\delta_2 + \frac{2}{3}\delta_6) \right\} + g \{ 1 - \frac{2}{3}\beta^2 + \frac{2}{3}\beta^4 - \beta^6 \} \right], \quad (8)$$

where  $g=1$ ,  $\delta_n = \beta^n - \alpha^n$ , when  $\psi^2 - 2\psi B - V \geq 0$ ,

$g=0$ ,  $\delta_n = 1 - \alpha^n$ , when  $\psi^2 - 2\psi B - V < 0$ .

This value of  $f_1$  refers to the fraction  $p$  of the electrons which have at the instant under consideration orbital energy  $B^2$  and binding energy  $V$ .

In the case of electrons which move in elliptic-like orbits the orbital kinetic energy varies continuously between certain limits, and in order to obtain the exact contribution of the whole orbit it is necessary to make an integration. As  $B$  enters in a complicated way into  $f_1$  the integration would probably be difficult. The value of  $f_1$  for electrons moving in elliptic-like orbits can, however, be obtained with sufficient accuracy by dividing the range of values of  $B$  into finite intervals and then making a summation. For this purpose the intervals defined by  $r' = \frac{1}{5}, \frac{2}{5}, \frac{3}{5}, \frac{4}{5}$ , and 1 have been chosen,  $r'$  being the distance of the electron from the nucleus expressed as a fraction of the maximum values of that distance. The kinetic energy of an electron at a point in its orbit defined by the azimuthal angle  $\gamma$  is proportional to

$$[1 + e^2 + 2e \cos \gamma],$$

and is approximately equal to

$$V \times [1 + e^2 + 2e \cos \gamma] / 1 - e^2,$$

$e$  being the eccentricity of the elliptic orbit and  $V$  the

binding energy of the electron\*. This expression gives the value of  $B^2$  in any interval, so that from (8) the value of  $f_1$  for the electrons concerned can be calculated. In calculating the value of  $f_1$  for circular orbits, the kinetic energy of the electron is taken to be equal to the binding energy, which is approximately true.

The quantity  $f$ , whose value we require, is the fraction of the total number of quanta scattered by an atom of the element, which produces recoil electrons that can escape from the atom. The contribution of any class of electrons which constitutes a fraction  $p$  of the total number of electrons in the atom is evidently  $f_1 \times p$ , so that  $f$  is given by

$$f = \sum f_1 p.$$

The values of  $f$  have been calculated for the different elements and different wave-lengths of X-rays used in the various experiments and are given in Table V. Bohr's distribution of the electrons amongst the various orbits has been assumed and the values of  $V$  have been obtained from curves given by K. T. Compton and F. L. Mohler †.

TABLE V.

Gas.	Assumed distributions of electrons in the atoms, and the values of $V$ (in volts).	Wave-length.	$f$ .
Oxygen ...	2K, $V=500$ : 4L <sub>21</sub> , $V=50$ : 2L <sub>22</sub> , $V=14$	709 Å	816
"	" " "	614	843
"	" " "	545	866
"	" " "	57	855
"	" " "	35	935
Nitrogen..	2K, $V=381$ : 4L <sub>21</sub> , $V=41$ : 1L <sub>22</sub> , $V=11$	614	850
"	" " "	545	876
"	" " "	57	843
"	" " "	35	940
Argon.....	2K, $V=3200$ : 4L <sub>21</sub> , $V=540$ : 4L <sub>22</sub> , $V=410$ : } 4M <sub>21</sub> , $V=110$ ; 4M <sub>32</sub> , $V=26$ }	614	67
"	" " "	545	71
Hydrogen.	1K, $V=16$ .	614	971

## SUMMARY.

The Wilson cloud method has been used to investigate the short  $\beta$ -ray tracks produced in a gas traversed by X-rays which have been identified with recoil electrons associated with the scattering of the X-rays. In all the experiments

\* This expression for the kinetic energy depends on the assumption of the same effective nuclear charge for the calculation of the potential field and the nuclear attracting force.

† Compton and Mohler Bull. Nat. Res. Coun. 9 A, p. 1 (1924).

homogeneous X-rays, produced by reflexion from a crystal, have been used and about 300 stereoscopic pairs of photographs have been examined.

The results which have been obtained refer to the tracks produced in oxygen, nitrogen, and argon by X-rays of wave-lengths  $\cdot 709 \text{ \AA}^*$ ,  $\cdot 614 \text{ \AA}$ , and  $\cdot 545 \text{ \AA}$ , to those in hydrogen (containing small known percentages of other gases) by X-rays of wave-length  $\cdot 614 \text{ \AA}$ , and to those in air by rays of wave-lengths  $\cdot 57 \text{ \AA}$  and  $\cdot 35 \text{ \AA}$ .

The *distribution* of the short tracks produced in oxygen and nitrogen has been examined and found to be a random one, at least for those short tracks whose origins are separated by more than 1 mm. from the origins of the long tracks.

The ratio  $N_R/N_P$  of the number of short tracks to the number of long tracks, according to the theory, should be equal to the ratio of the scattering coefficient to the absorption coefficient multiplied by the fraction  $f$  of scattered quanta, which give sufficient energy to the scattering electrons to enable them to leave their parent atoms. The fraction,  $f$ , has been calculated on certain assumptions, and an expression obtained for it in terms of the binding energies of the electrons and the wave-length of the radiation. The theoretical values of the ratio  $N_R/N_P$  thus obtained are in satisfactory agreement with the observed values of this ratio, which vary from  $\cdot 029$  for argon and radiation of wave-length  $\cdot 545 \text{ \AA}$ , to  $3\cdot 5$  for hydrogen (containing a small percentage of oxygen) and rays of wave-length  $\cdot 614 \text{ \AA}$ . This consistent agreement over a wide range between the theoretical and observed values strongly supports the quantum theory of scattering and shows that all the scattered radiation obeys that theory. The experiments are being continued with X-rays of shorter wave-length.

In conclusion we should like to express our thanks to Professor C. T. R. Wilson, F.R.S., for his valuable advice on the technique of the method of cloud photography, and to Professor W. L. Bragg, F.R.S., for many helpful suggestions and for his continued interest in the work.

Manchester University,  
February 1926.

\* Oxygen only.

*CX. The Effect of Axial Restraint on the Stress in a Rotating Disk.* By W. G. GREEN, B.Sc., A.M.I.N.A.\*

§ 1. INTRODUCTION.

**T**HE problem on which light is sought is that of a rotating disk carried on a shaft, but a complete solution appears to be out of the question. One effect of the presence of the shaft is to prevent the parts of the disk that are near the axis shifting so far in the direction of the axis as they would if there were no shaft, and it is proposed to trace the consequences of this effect by solving an illustrative problem.

The case treated is that of a disk of outer radius  $a$ , and of thickness  $2h$ , the plane faces being represented by  $z = \pm h$ . It is assumed that the disk is restrained by concentrated axial tensions  $P$ , induced by rotation, at the centres of the outside faces. When such a disk rotates with angular velocity  $\omega$ , two stress-systems are produced, viz. :

- (A) That due to concentrated axial tensions  $P$ , in a complete disk at rest.
- (B) That due to rotation  $\omega$  in a complete disk under no superficial tractions.

For the first, it is essential to regard the radius of the disk as infinite, but the results obtained, however, show that the error due to this assumption is small. For the second, Chree's solution† will be taken. By compounding these two stress-systems, the total stress-components and displacements can be determined. For the determination of  $P$  in terms of  $\omega$ , it will be assumed that the axial displacement  $w=0$  when  $z = \pm h$ ,  $r=r_1$ , where  $r_1$  may be taken to represent the radius of the shaft.

Before developing the analysis on the lines of the résumé given above, it is necessary to mention the stresses arising from a concentrated force acting at a point on the plane boundary of an elastic solid.

\* Communicated by Prof. A. E. H. Love.

† A. E. H. Love, 'Mathematical Theory of Elasticity,' 3rd edn. § 102. Case (b).

§ 2. PRESSURE AT A POINT ON A PLANE BOUNDARY \*.

Taking the origin to be the point at which the load is applied, the plane  $z=0$  to be the bounding surface of the body, and the positive direction of the axis of  $z$  to be that which passes into the interior of the body, then, expressing the results in cylindrical coordinates, the tractions across a plane parallel to the plane boundary are

$$\widehat{z z} = \frac{3P}{2\pi} \cdot \frac{z^3}{(z^2 + r^2)^{5/2}}, \quad \dots \quad (1)$$

$$\widehat{z r} = \frac{3P}{2\pi} \cdot \frac{z^2 r}{(z^2 + r^2)^{5/2}}, \quad \dots \quad (2)$$

where  $P$  is the applied load, and is positive for tension,

$\widehat{z z}$  is the direct stress parallel to the direction of  $P$ ,

$\widehat{z r}$  is the shear stress in planes passing through the line of action of  $P$ .

It will be necessary to express these tractions in terms of definite integrals involving Bessel's Functions, of order zero and unity respectively. The required expressions can be deduced easily from the well-known result

$$\int_0^\infty e^{-kz} J_0(kr) dk = (r^2 + z^2)^{-1/2} \quad \dots \quad (3)$$

by differentiation, with respect to  $z$  and  $r$ , under the sign of integration. Hence it follows that

$$\widehat{z z} = \frac{P}{2\pi} \int_0^\infty k(1 + kz) e^{-kz} J_0(kr) dk, \quad \dots \quad (4)$$

$$\widehat{z r} = \frac{P}{2\pi} \int_0^\infty k^2 z e^{-kz} J_1(kr) \cdot dk. \quad \dots \quad (5)$$

Using these results, the stress-system due to concentrated axial tensions  $P$ , in a complete disk at rest, can be developed.

§ 3. THE STRESS-SYSTEM (A), DUE TO CONCENTRATED AXIAL TENSIONS  $P$ , IN A COMPLETE DISK AT REST.

(a) It is convenient to subdivide this system into three component systems as follows:—

\* Love, *op. cit.* § 135.



- I. That due to an axial tension  $P$ , acting at the surface of an infinite solid bounded by the plane  $z = -h$ , and lying on the side  $z > -h$  of this plane.

Here equations (4) and (5) become

$$\widehat{z}_1 = \frac{P}{2\pi} \int_0^\infty k \{1 + k(h+z)\} e^{-k(h+z)} J_0(kr) dk, \quad (6)$$

$$\widehat{z}r_1 = \frac{P}{2\pi} \int_0^\infty k^2 (h+z) e^{-k(h+z)} J_1(kr) dk, \quad (7)$$

giving stress-components at  $z = h$

$$\widehat{z}_1 = \frac{P}{2\pi} \int_0^\infty k(1 + 2hk) e^{-2hk} J_0(kr) dk, \quad (8)$$

$$\widehat{z}r_1 = \frac{P}{2\pi} \int_0^\infty 2hk^2 e^{-2hk} J_1(kr) dk. \quad (9)$$

- II. That due to an axial tension  $P$ , acting at the surface of an infinite solid bounded by the plane  $z = h$ , and lying on the side  $z < h$  of this plane. In this case equations (4) and (5) become

$$\widehat{z}_2 = \frac{P}{2\pi} \int_0^\infty k \{1 + k(h-z)\} e^{-k(h-z)} J_0(kr) dk, \quad (10)$$

$$\widehat{z}r_2 = -\frac{P}{2\pi} \int_0^\infty k^2 (h-z) e^{-k(h-z)} J_1(kr) dk, \quad (11)$$

giving stress-components at  $z = -h$

$$\widehat{z}_2 = \frac{P}{2\pi} \int_0^\infty k(1 + 2hk) e^{-2hk} J_0(kr) dk, \quad (12)$$

$$\widehat{z}r_2 = -\frac{P}{2\pi} \int_0^\infty 2hk^2 e^{-2hk} J_1(kr) dk. \quad (13)$$

- III. The system in the infinite slab contained between the planes  $z = \pm h$ , these planes being subject to tractions obtained by reversing the components  $\widehat{z}z$  and  $\widehat{z}r$  at  $z = h$  in I, and at  $z = -h$  in II.

By compounding the systems I, II, and III, the stress-components in the complete disk at rest, due to the concentrated axial tensions  $P$ , can be determined.

### (b) Determination of the Stress-Components.

For symmetrical strain in a solid of revolution\*, the results may be expressed in terms of a function  $\chi$  which

\* Love, *op. cit.* § 188.

satisfies the differential equation  $\nabla^4 \chi = 0$ , where

$$\nabla^2 \chi \equiv \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} \right) \equiv \left( \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} \right).$$

The stress-components are then given by

$$\left. \begin{aligned} \hat{r}r &= \frac{\partial}{\partial z} \left[ \sigma \cdot \nabla^2 \chi - \frac{\partial^2 \chi}{\partial r^2} \right], \\ \hat{\theta}\theta &= \frac{\partial}{\partial z} \left[ \sigma \cdot \nabla^2 \chi - \frac{1}{r} \frac{\partial \chi}{\partial r} \right], \\ \hat{z}z &= \frac{\partial}{\partial z} \left[ (2-\sigma) \nabla^2 \chi - \frac{\partial^2 \chi}{\partial z^2} \right], \end{aligned} \right\} \dots (14)$$

$$\hat{z}r = \frac{\partial}{\partial r} \left[ (1-\sigma) \cdot \nabla^2 \chi - \frac{\partial^2 \chi}{\partial z^2} \right], \dots (15)$$

and the displacements by

$$\left. \begin{aligned} u &= -\frac{1+\sigma}{E} \cdot \frac{\partial^2 \chi}{\partial r \partial z}, \\ w &= \frac{1+\sigma}{E} \cdot \left[ (1-2\sigma) \nabla^2 \chi + \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \chi}{\partial r} \right]. \end{aligned} \right\} \dots (16)$$

A solution for  $\chi$  may be written

$$\chi = \Sigma J_0(kr) \left[ \left( C + \frac{z}{2k} \cdot A \right) e^{kz} + \left( D - \frac{z}{2k} \cdot B \right) e^{-kz} \right],$$

where

$$\nabla^2 \chi = \Sigma J_0(kr) [A e^{kz} + B e^{-kz}],$$

the summation being for any number of values of  $k$ ; A, B, C, and D being arbitrary constants.

In the stress-system due to pressure at a point on a plane boundary, § 2, A and C are both zero, and it can be readily shown that the value

$$\chi = \frac{P}{2\pi} \int_0^\infty \frac{1}{k^2} [\{2\sigma + kz\} e^{-kz} J_0(kr) - \{2\sigma + kz(1-2\sigma)\}] dk, \dots (17)$$

together with equations (14) and (15), will give correctly the expressions for  $\hat{z}z$  and  $\hat{z}r$ , equations (4) and (5).

Again, in the stress-system III, due to the reversed tractions,  $C = -D$ ,  $A = -B$ , giving a symmetrical solution.

Using these results it is now possible to write down the functions  $\chi_1$ ,  $\chi_2$ ,  $\chi_3$ , representing the systems I, II, and III, respectively, and rearranging the constants in the latter case,

we have

$$\chi_1 = \frac{P}{2\pi} \int_0^\infty \frac{1}{k^3} [\{2\sigma + k(h+z)\} e^{-k(h+z)} J_0(kr) - \{2\sigma + (1-2\sigma)k(h-z)\}] dk, \quad (18)$$

$$\chi_2 = -\frac{P}{2\pi} \int_0^\infty \frac{1}{k^3} [\{2\sigma + k(h-z)\} e^{-k(h-z)} J_0(kr) - \{2\sigma + (1-2\sigma)k(h-z)\}] dk, \quad (19)$$

$$\chi_3 = \frac{P}{\pi} \int_0^\infty \frac{1}{k^3} [(\alpha \sinh kz - \beta k z \cosh kz) J_0(kr) - (\alpha - \beta) k z] dk. \quad (20)$$

The linear functions of  $z$ , included in the above expressions, secure that the integral is convergent in each case.

(c) *Evaluation of the Stress-Components I.*

From equation (18) it follows that

$$\left. \begin{aligned} \frac{1}{r} \frac{\partial \chi_1}{\partial r} &= -\frac{P}{2\pi} \int_0^\infty \{2\sigma + k(h+z)\} e^{-k(h+z)} \frac{J_1(kr)}{(kr)} dk, \\ \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \chi_1}{\partial r} &= -\frac{P}{2\pi} \int_0^\infty \{2\sigma + k(h+z)\} e^{-k(h+z)} J_0(kr) dk, \\ \frac{\partial^2 \chi_1}{\partial z^2} &= -\frac{P}{2\pi} \int_0^\infty \{2(1-\sigma) - k(h+z)\} e^{-k(h+z)} J_0(kr) dk, \\ \nabla^2 \chi_1 &= -\frac{P}{\pi} \int_0^\infty e^{-k(h+z)} J_0(kr) dk. \end{aligned} \right\} \quad (21)$$

Substituting in equations (14), and using the relation

$$\frac{\partial^2 \chi}{\partial r^2} = \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \chi}{\partial r} - \frac{1}{r} \frac{\partial \chi}{\partial r},$$

the stress-components may be written

$$\left. \begin{aligned} \hat{r}r_1 &= \frac{P}{2\pi} \int_0^\infty e^{-k(h+z)} \left[ 2\sigma \cdot \frac{J_1(kr)}{kr} + \{1 - k(h+z)\} \left\{ J_0(kr) - \frac{J_1(kr)}{kr} \right\} \right] k dk, \\ \hat{\theta}\theta_1 &= \frac{P}{2\pi} \int_0^\infty e^{-k(h+z)} \left[ \{1 - k(h+z)\} \frac{J_1(kr)}{kr} + 2\sigma \left\{ J_0(kr) - \frac{J_1(kr)}{kr} \right\} \right] k dk, \\ \hat{z}z_1 &= \frac{P}{2\pi} \int_0^\infty e^{-k(h+z)} \{1 + k(h+z)\} J_0(kr) k dk. \end{aligned} \right\} \quad (22)$$

These components may be evaluated graphically, in the manner used for the stress-system III, to be described later. The component  $\widehat{z}z_1$  is, however, given directly by equation (1), and may be written

$$\widehat{z}z_1 = \frac{3P}{2\pi} \cdot \frac{(h+z)^3}{\{(h+z)^2 + r^2\}^{5/2}} \quad \dots \quad (23)$$

The components  $\widehat{r}r_1$  and  $\theta\theta_1$  can also be calculated directly by using Polar Coordinates\*. See Appendix.

A similar set of expressions can be developed for the stress-system II, but the results are easily obtained from those already given.

(d) *Evaluation of the Stress-Components III.*

Proceeding as before, equation (20) gives

$$\left. \begin{aligned} \frac{1}{r} \frac{\partial \chi_3}{\partial r} &= -\frac{P}{\pi} \int_0^\infty \{ \alpha \sinh kz - \beta kz \cosh kz \} \frac{J_1(kr)}{kr} dk, \\ \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \chi_3}{\partial r} &= -\frac{P}{\pi} \int_0^\infty \{ \alpha \sinh kz - \beta kz \cosh kz \} J_0(kr) dk, \\ \frac{\partial^2 \chi_3}{\partial z^2} &= \frac{P}{\pi} \int_0^\infty \{ (\alpha - 2\beta) \sinh kz \\ &\quad - \beta kz \cosh kz \} J_0(kr) dk, \\ \nabla^2 \chi_3 &= -\frac{P}{\pi} \int_0^\infty 2\beta \sinh kz J_0(kr) dk. \end{aligned} \right\} \quad \dots \quad (24)$$

So that substituting in equations (14) and (15), as before, the stress-components become

$$\left. \begin{aligned} \widehat{r}r_3 &= -\frac{P}{\pi} \int_0^\infty \left[ 2\beta \sigma \cosh kz \cdot J_0(kr) - J_0(kr) - \frac{J_1(kr)}{kr} \right] \\ &\quad \times \{ (\alpha - \beta) \cosh kz - \beta kz \sinh kz \} k dk, \\ \widehat{\theta}\theta_3 &= -\frac{P}{\pi} \int_0^\infty \left[ 2\beta \sigma \cosh kz \cdot J_0(kr) - \frac{J_1(kr)}{kr} \right] \\ &\quad \times \{ (\alpha - \beta) \cosh kz - \beta kz \sinh kz \} k dk, \\ \widehat{z}z_3 &= -\frac{P}{\pi} \int_0^\infty \left[ \{ \alpha + \beta(1 - 2\sigma) \} \cosh kz - \beta kz \sinh kz \right] \\ &\quad \times J_0(kr) k dk, \end{aligned} \right\} \quad \dots \quad (25)$$

\* Love, *op. cit.* § 142, Case (i). Putting  $\alpha = \frac{\pi}{2}$ , we obtain the solution for pressure at a point on a plane boundary, expressed in Polar Coordinates.

$$\widehat{zr}_3 = -\frac{P}{\pi} \int_0^\infty \left[ \beta k z \cosh kz - (\alpha - 2\beta\sigma) \sinh kz \right] J_1(kr) k dk. \quad (26)$$

Now the condition for the determination of the constants  $\alpha$  and  $\beta$  is obtained by reversing the tractions I at  $z=h$ , or the tractions II at  $z=-h$ . Hence, at  $z=h$ , we must have

$$\widehat{zr}_3 = -\widehat{zr}_1,$$

$$\widehat{zz}_3 = -\widehat{zz}_1,$$

so that, combining equations (8) and (9) with the expressions for  $zz_3$ , and  $\widehat{zr}_3$ , when  $z=h$ , given by equations (25) and (26), we have, for a particular value of  $k$ ,

$$\{\alpha + \beta(1 - 2\sigma)\} \cosh kh - \beta kh \sinh kh = \frac{1 + 2hk}{2} \cdot e^{-2hk},$$

$$\beta kh \cdot \cosh kh - (\alpha - 2\beta\sigma) \sinh kh = hk \cdot e^{-2hk}.$$

Solving these equations for  $\alpha$  and  $\beta$ , the latter become

$$\alpha = e^{-2hk} \cdot \frac{\left[ \begin{array}{l} \{2\sigma(1 + 2hk) + 2h^2k^2\} \sinh kh \\ \{hk(1 + 2hk) - 2hk(1 - 2\sigma)\} \cosh kh \end{array} \right]}{2hk + \sinh 2hk}, \quad (27)$$

$$\beta = e^{-2hk} \cdot \frac{[(1 + 2hk) \sinh kh + 2hk \cosh kh]}{2hk + \sinh 2hk}. \quad (28)$$

These expressions show  $\alpha$  and  $\beta$  to be functions of  $hk$ , and, assuming Poisson's Ratio  $\sigma = .3$ , calculated values of these constants are given in Table I.

TABLE I.

$hk.$	$\alpha.$	$\beta.$
0 .....	.200	.750
.25 .....	.262	.531
.50 .....	.265	.368
1.0 .....	.1891	.1592
1.5 .....	.0995	.0595
2.0 .....	.0418	.0194
3.0 .....	.00489	.001535
4.0 .....	.000428	.0001036

The stress-components, given by equations (25), can now be evaluated graphically. The integrals, in every case, may be expressed as functions of  $hk$ , by taking points whose coordinates  $r, z$ , are multiples, or sub-multiples, of  $h$ . Using the tabulated values of  $\alpha$  and  $\beta$ , and the appropriate values of Bessel's Functions\*, the subject of integration can be calculated for definite values of  $hk$ , and a curve drawn showing the variation of this function with  $hk$ . The area under the curve having been determined, by means of a planimeter, or otherwise, we can then write

$$\text{Stress-Component} = \delta_3 \frac{P}{\pi h^2},$$

where  $\delta_3$  is a numerical constant, representing the stress components in system III. Taking  $\sigma = .3$ , as before, values of  $\delta_3$  are given in Table II.

TABLE II.

	Plane $z = 0$ .			Plane $z = \frac{h}{2}$ .			Plane $z = h$ .		
	$\widehat{rr}_3$ .	$\widehat{\theta\theta}_3$ .	$\widehat{zz}_3$ .	$\widehat{rr}_3$ .	$\widehat{\theta\theta}_3$ .	$\widehat{zz}_3$ .	$\widehat{rr}_3$ .	$\widehat{\theta\theta}_3$ .	$\widehat{zz}_3$ .
$r = 0$ .....	-.133	-.133	-.417	-.186	-.186	-.430	-.474	-.474	-.375
$r = \frac{h}{2}$ .....	-.133	-.124	-.368	-.172	-.176	-.372	-.372	-.405	-.322
$r = h$ .....	-.126	-.102	-.259	-.148	-.137	-.251	-.206	-.276	-.215
$r = 2h$ .....	-.084	-.062	-.075	-.073	-.070	-.070	-.017	-.088	-.066
$r = 3h$ .....	-.036	-.034	-.011	-.026	-.039	-.013	-.000	-.040	-.020

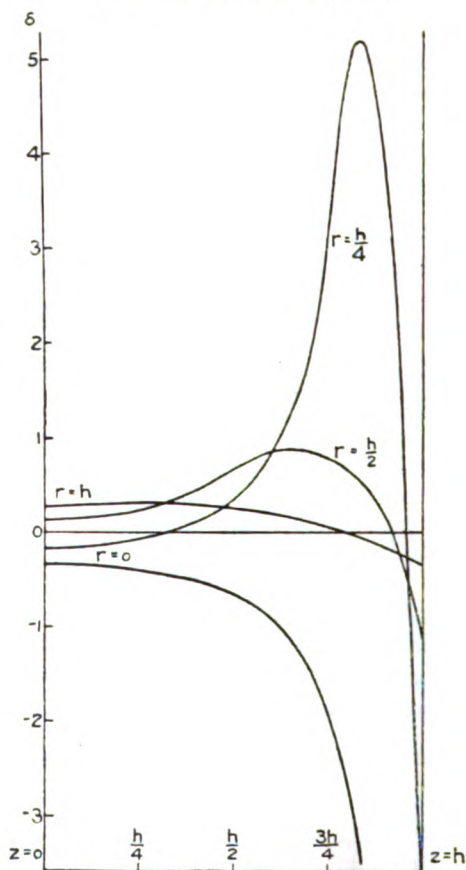
(e) *Calculated Values of the Stress-Components in the complete disk at rest.*

The stress-components I and II, for points corresponding to those taken in system III, have been calculated, using Polar Coordinates for the  $\widehat{rr}$ ,  $\widehat{\theta\theta}$  values, as already indicated. Reducing them to the same form as before, these components

\* Jahnke and Emde, 'Funktionentafeln mit Formeln und Kurven,' Teubner, 1909.

TABLE III.

	Plane $z = 0$ .			Plane $z = \frac{h}{2}$ .			Plane $z = h$ .		
	$\widehat{rr}$ .	$\widehat{\theta\theta}$ .	$\widehat{zz}$ .	$\widehat{rr}$ .	$\widehat{\theta\theta}$ .	$\widehat{zz}$ .	$\widehat{rr}$ .	$\widehat{\theta\theta}$ .	$\widehat{zz}$ .
$r = 0$ .....	-.333	-.333	2.583	-.630	-.630	6.237	—	—	—
$r = \frac{h}{2}$ .....	.128	-.240	1.348	.671	-.259	1.201	-1.176	.373	0
$r = h$ .....	.287	-.126	.271	.260	-.116	.122	-.373	-.089	0
$r = 2h$ .....	.076	-.042	-.021	.041	-.046	-.013	-.015	-.041	0
$r = 3h$ .....	.019	-.016	-.002	.017	-.020	-.000	.015	-.019	0

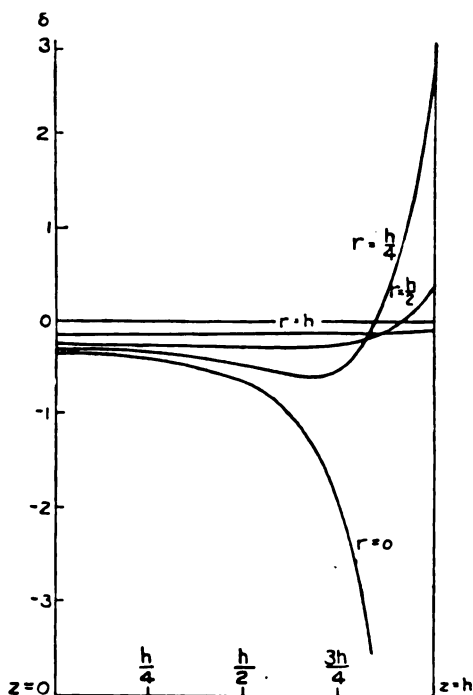
Fig. 1.— $\delta$  Values for Component  $rr$ .

may be represented by numerical constants  $\delta_1$  and  $\delta_2$ . Compounding the three systems, and writing

$$\delta = \delta_1 + \delta_2 + \delta_3,$$

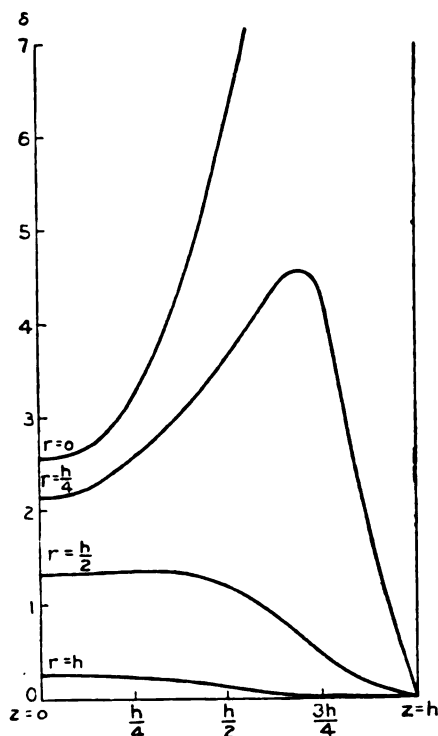
values of  $\delta$ , representing the stress-components in the complete disk at rest, are given in Table III., and in figs. 1, 2, and 3.

Fig. 2.— $\delta$  Values for Component  $\theta\theta$ .



It should be remembered that the expressions giving the stresses arising from "pressure at a point on a plane boundary" are true for all points not too near the origin, when the pressure is applied at the origin. Hence the above analysis is true for all points not too near the centres of the outside faces of the disk.



Fig. 3.— $\delta$  Values for Component  $\widehat{zz}$ .

## § 4. THE STRESS-SYSTEM (B) DUE TO ROTATION ONLY.

The results of the solution due to Chree \* are summarized below for convenience. The stress-components are given by

$$\left. \begin{aligned} \widehat{rr} &= \frac{\rho\omega^2}{8} (3 + \sigma)(a^2 - r^2) + \frac{\rho\omega^2}{6} \cdot \sigma \cdot \frac{1 + \sigma}{1 - \sigma} (h^2 - 3z^2), \\ \widehat{\theta\theta} &= \frac{\rho\omega^2}{8} \{ (3 + \sigma)a^2 - (1 + 3\sigma)r^2 \} + \frac{\rho\omega^2}{6} \sigma \cdot \frac{1 + \sigma}{1 - \sigma} (h^2 - 3z^2), \\ \widehat{zz} &= \widehat{zr} = 0, \end{aligned} \right\} \dots (29)$$

\* Love, *op. cit.* § 102, Case (b).

and the displacements by

$$\left. \begin{aligned} u &= \frac{\rho \omega^2 r}{8E} (1-\sigma) \{ (3+\sigma) a^2 - (1+\sigma) r^2 \} \\ &\quad + \frac{\rho \omega^2 \cdot r}{6E} \sigma (1+\sigma) (h^2 - 3z^2), \\ w &= -\frac{\rho \omega^2 z}{4E} \cdot \sigma \{ (3+\sigma) a^2 - 2(1+\sigma) r^2 \} \\ &\quad - \frac{\rho \omega^2 z}{3E} \sigma^2 \cdot \frac{1+\sigma}{1-\sigma} (h^2 - z^2). \end{aligned} \right\} \quad \dots (30)$$

### § 5. DETERMINATION OF THE AXIAL TENSIONS.

(a) *Axial displacements in the Stress-System A.*

Equation (16) gives the axial displacement  $w$  in terms of the function  $\chi$ .

Now

$$\left. \begin{aligned} \nabla^2 \chi_1 &= -\frac{P}{\pi} \int_0^\infty e^{-k(h+z)} J_0(kr) dk, \\ \nabla^2 \chi_2 &= \frac{P}{\pi} \int_0^\infty e^{-k(h-z)} J_0(kr) dk, \\ \nabla^2 \chi_3 &= -\frac{P}{\pi} \int_0^\infty 2\beta \sinh kz J_0(kr) dk, \end{aligned} \right\} \quad \dots (31)$$

and

$$\left. \begin{aligned} \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \chi_1}{\partial r} &= -\frac{P}{2\pi} \int_0^\infty e^{-k(h+z)} J_0(kr) \{ 2\sigma + k(h+z) \} dk, \\ \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \chi_2}{\partial r} &= \frac{P}{2\pi} \int_0^\infty e^{-k(h-z)} J_0(kr) \{ 2\sigma + k(h-z) \} dk, \\ \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \chi_3}{\partial r} &= -\frac{P}{\pi} \int_0^\infty \{ \alpha \sinh kz - \beta kz \cosh kz \} J_0(kr) dk. \end{aligned} \right\} \quad \dots (32)$$

Substituting in equation (16), the displacements are given by

$$\left. \begin{aligned} w_1 &= -\frac{P}{2\pi} \cdot \frac{1+\sigma}{E} \int_0^\infty e^{-k(h+z)} J_0(kr) \{ 2(1-\sigma) + k(h+z) \} dk, \\ w_2 &= \frac{P}{2\pi} \cdot \frac{1+\sigma}{E} \int_0^\infty e^{-k(h-z)} J_0(kr) \{ 2(1-\sigma) + k(h-z) \} dk, \\ w_3 &= -\frac{P}{\pi} \cdot \frac{1+\sigma}{E} \int_0^\infty [ \{ \alpha + 2\beta(1-2\sigma) \} \sinh kz - \beta kz \cosh kz ] \\ &\quad J_0(kr) dk. \end{aligned} \right\} \quad \dots (33)$$

Putting  $z=h$ ,  $r=r_1$ , these become

$$\left. \begin{aligned} w_1 &= -\frac{P}{\pi h} \cdot \frac{1+\sigma}{E} \int_0^\infty e^{-2kh} J_0(kr_1) \{(1-\sigma) + kh\} d(kh), \\ w_2 &= \frac{P}{\pi r_1} \cdot \frac{1-\sigma^2}{E}, \\ w_3 &= -\frac{P}{\pi h} \cdot \frac{1+\sigma}{E} \int_0^\infty [\{\epsilon + 2\beta(1-2\sigma)\} \sinh kh - \beta kh \cosh kh] \\ &\quad \times J_0(kr_1) d(kh). \end{aligned} \right\} \quad \dots (34)$$

Expressing these displacements in the form

$$w_1 = \gamma_1 \cdot \frac{P}{\pi h E} \text{ etc. } \dots (35)$$

$$\text{where } \gamma = \gamma_1 + \gamma_2 + \gamma_3,$$

and integrating  $w_1$  and  $w_3$  graphically, numerical values of  $\gamma$  are given in Table IV.

TABLE IV.

	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma$
$r_1 = \frac{h}{4}$ .....	-774	3.640	-272	2.594
$r_1 = \frac{h}{2}$ .....	-754	1.820	-243	.823
$r_1 = \frac{3h}{4}$ .....	-712	1.213	-203	.298
$r_1 = h$ .....	-646	.910	-156	.108

(b) *Determination of P.*

The condition of restraint assumed is that the resultant axial displacement vanishes at  $z=\pm h$ ,  $r=r_1$ . Due to pure rotation, the axial displacement at  $z=h$ ,  $r=r_1$  is given by equation (30), and is

$$w = -\frac{\rho\omega^2 h}{4E} \sigma \{(3+\sigma)a^2 - 2(1+\sigma)r_1^2\}. \dots (36)$$

The displacements given by equations (35) and (36) must

therefore neutralize each other, hence

$$\frac{P}{\pi h^2} = \rho \omega^2 a^2 \frac{\sigma}{4\gamma} \left\{ (3 + \sigma) - 2(1 + \sigma) \frac{r_1^2}{a^2} \right\}, \quad (37)$$

and if  $\sigma = \cdot 3$  this gives

$$\frac{P}{\pi h^2} = \frac{\rho \omega^2 a^2}{\gamma} \left\{ \cdot 2475 - \cdot 195 \frac{r_1^2}{a^2} \right\}. \quad (38)$$

## § 6. TOTAL STRESS-COMPONENTS WHEN ROTATING UNDER RESTRAINT.

These are obtained by compounding the stress-systems A and B. In the former we can now write

$$\text{Stress-Component} = \delta \frac{P}{\pi h^2} = \rho \omega^2 a^2 \frac{\delta}{\gamma} \left\{ \cdot 2475 - \cdot 195 \frac{r_1^2}{a^2} \right\}. \quad (39)$$

Values of  $\delta$  are given by Table III. and the accompanying diagrams. For a given value of  $r_1$  the appropriate value of  $\gamma$  can be determined from the results given in Table IV. Thus, equation (39) gives the stress-component at any point in the system A, for any assumed condition of restraint.

For the stress-system B, equations (29) determine the stress-components at any point.

To illustrate the effect of restraint, consider the case when  $r_1 = \frac{h}{2}$ . The value of  $\gamma$  given by Table IV. is  $\cdot 823$ , and so equation (39) becomes

$$\text{Stress-Component} = \rho \omega^2 a^2 \cdot \delta \left\{ \cdot 301 - \cdot 0593 \frac{h^2}{a^2} \right\}. \quad (40)$$

Further, considering the stresses at the point  $r = \frac{h}{2}$ ,  $z = \frac{h}{2}$ , and substituting the appropriate values of  $\delta$ , given in Table III., we have, in the stress-system A,

$$\left. \begin{aligned} \widehat{rr} &= \rho \omega^2 a^2 \left\{ \cdot 202 - \cdot 0398 \frac{h^2}{a^2} \right\}, \\ \widehat{\theta\theta} &= - \rho \omega^2 a^2 \left\{ \cdot 078 - \cdot 0154 \frac{h^2}{a^2} \right\}, \\ \widehat{zz} &= \rho \omega^2 a^2 \left\{ \cdot 362 - \cdot 0713 \frac{h^2}{a^2} \right\}, \end{aligned} \right\} \quad (41)$$

For the stress-system B, when  $r = \frac{h}{2}$ ,  $z = \frac{h}{2}$ , equations (29) give

$$\left. \begin{aligned} \widehat{rr} &= \rho\omega^2 a^2 \left\{ .4125 - .0799 \frac{h^2}{a^2} \right\}, \\ \widehat{\theta\theta} &= \rho\omega^2 a^2 \left\{ .4125 - .0362 \frac{h^2}{a^2} \right\}, \\ \widehat{zz} &= 0. \end{aligned} \right\} \quad \cdot \cdot \quad (42)$$

The total stress-components, at  $r = \frac{h}{2}$ ,  $z = \frac{h}{2}$ , are therefore

$$\left. \begin{aligned} \widehat{rr} &= \rho\omega^2 a^2 \left\{ .6145 - .1197 \frac{h^2}{a^2} \right\}, \\ \widehat{\theta\theta} &= \rho\omega^2 a^2 \left\{ .3345 - .0208 \frac{h^2}{a^2} \right\}, \\ \widehat{zz} &= \rho\omega^2 a^2 \left\{ .362 - .0713 \frac{h^2}{a^2} \right\}. \end{aligned} \right\} \quad \cdot \cdot \quad (43)$$

Similar expressions may be obtained for all points.

### § 7. THE EFFECT OF THE RADIUS OF THE SHAFT.

The greater the diameter of the shaft, the more effective it becomes in restricting the axial movement of parts of the disk that are near the axis. This effect is shown clearly by the variation in the value of  $\gamma$  for different values of  $r_1$  given in Table IV. The theory is limited, however, by the fact that the effect of the shaft is not concentrated, and the result of this distribution is that, for values of  $r$  less than  $r_1$ , the stress-components tend to definite finite limits on approaching the planes  $z = \pm h$ , instead of tending to infinite and zero values as shown in figs. 1, 2, and 3. It should be borne in mind that the assumption of concentrated axial tensions is merely a means of effecting restraint, and in a disk carried on a shaft of radius  $r_1$ , the theory indicates the stress distribution for values of  $r$  equal to or greater than  $r_1$ . A more complete application of the foregoing analysis to practical conditions, although of great importance, should hardly, perhaps, be considered here, and might with advantage be dealt with subsequently.

APPENDIX.

*Pressure at a point on a plane boundary, referred to Polar Coordinates\*.*

Referred to Polar Coordinates, the stress-components are expressed by the equations

$$\left. \begin{aligned} \widehat{rr} &= \frac{P}{2\pi r^2} (1-2\sigma) \left[ \frac{2(2-\sigma)}{(1-2\sigma)} \cos \theta - 1 \right], \\ \widehat{\theta\theta} &= -\frac{P}{2\pi r^2} (1-2\sigma) \cdot \frac{\cos^2 \theta}{1 + \cos \theta}, \\ \widehat{\phi\phi} &= \frac{P}{2\pi r^2} (1-2\sigma) \left[ \frac{1}{1 + \cos \theta} - \cos \theta \right], \end{aligned} \right\} \quad (i.)$$

$$r\theta = -\frac{P}{2\pi r^2} (1-2\sigma) \frac{\sin \theta \cdot \cos \theta}{1 + \cos \theta}, \quad \dots \quad (ii.)$$

where, as in § 2, the origin is the point at which the load is applied, the axis being the line  $\theta=0$ , and the positive direction of  $r$  is that which goes into the interior of the body.

The component  $\widehat{\theta\theta}$ , expressed by Cylindrical Coordinates, is the component  $\widehat{\phi\phi}$  of equations (i.), and the component  $\widehat{rr}$ , of the preceding analysis, may be expressed in terms of Polar Coordinates by writing

$$\text{Radial Component} = \widehat{rr} \sin^2 \theta + \widehat{\theta\theta} \cos^2 \theta + \widehat{r\theta} \sin 2\theta \dagger, \quad (iii.)$$

where  $\widehat{rr}$ ,  $\widehat{\theta\theta}$ ,  $\widehat{r\theta}$  are given by equations (i.) and (ii.).

In conclusion, the writer wishes to record his indebtedness to Professor Love for the helpful suggestions and advice he has received relative to the solution of this problem.

R.N. Engineering College,  
Keyham, Devonport,  
February 1926.

\* See footnote, p. 1241.

† Love, *op. cit.* § 49.

CXI. *Determination of Surface-Tension by the Method of Ripples.* By P. N. GHOSH, D. BANERJI, and S. K. DATTA \*.

[Plate XXI.]

1. *Introduction.*

**L**ORD RAYLEIGH † developed the method of measuring the surface-tension of water by causing a thin blade of glass attached to one of the prongs of a tuning-fork of known frequency to excite ripples on its surface. These ripples were then viewed stroboscopically through a slit attached to the prongs of another fork of submultiple frequency. For keeping the amplitude within a low limit and at the same time to observe the ripples distinctly, the well-known Foucault arrangement was used to illuminate the surface of water on which the ripples are excited. Observing such stationary ripples in the direction of their propagation, they appear as alternate dark and bright bands, the distance between two consecutive dark or bright bands giving the wave-length.

The theory of such travelling ripples was worked on a hydrodynamical basis by Lord Kelvin ‡, and is expressed by the formula :—

$$\sigma = \frac{\lambda^3 n^2 \rho}{2\pi} - \frac{g \lambda^2 \rho}{4\pi^2},$$

where

$\sigma$  = surface-tension,

$\lambda$  = wave-length,

$n$  = frequency of the fork,

$\rho$  = density of the liquid.

The ripple method has since then been worked by Dorsey §, Grunmach ||, Kalähne ¶, Brummer \*\*, Kolowrat-Tscherinsky †† in determining surface-tension of water.

Owing to the difficulty of the stroboscopic arrangement, Grunmach and others produced stationary wave-patterns by the superposition of two systems of waves produced by fine styles attached to the two prongs of the fork.

\* Communicated by the Authors.

† Lord Rayleigh, *Scientific Papers*, vol. iii. pp. 383-396.

‡ Lord Kelvin, *Math. and Physical Papers*, vol. iv. & *Phil. Mag.* (4), xlii. p. 368 (1871).

§ Dorsey, *Phil. Mag.* (5), xlii. p. 369 (1897).

|| Grunmach, *Ann. der Physik*, ix. p. 1283 (1902).

¶ Kalähne, *Ann. der Physik*, vii. p. 462 (1902).

\*\* Brummer, *Rostock Dissert.*, 1903.

†† Kolowrat-Tscherinsky, *Journal d. russ Phys. Chem. Ges.* xxxvi. p. 265 (1904).

The main difficulties in the Rayleigh arrangement are the following :—

(1) The stroboscopic arrangement was not perfect, as slight disagreement in frequency relations between the exciting and the viewing fork affects the stationary character of the ripples, producing a variation in the position and width of the bright and dark bands.

(2) The estimation of  $\lambda$  by measuring appliances other than by an accurate micrometer is liable to lead to errors, which magnify themselves in the final computation of  $\sigma$ .

(3) The frequency of the exciting fork should be determined accurately while it is exciting the ripples. The frequency of the fork is modified owing to the contact of the liquid-surface, and as the square of the frequency occurs in the calculation of the surface-tension, a slight error in the estimation of this factor modifies the result considerably.

As to the methods of interference used by other workers, it is to be pointed out that the formation of true capillary ripples depends on the smallness of the amplitude of excitation. Unless, however, the intensity of the two sets of waves attains an appreciable value, the interference pattern is hardly perceptible, leading to uncertainty in the measurement of wave-length.

Some preliminary experiments to find out the effect of amplitude of the ripples and the value of the surface-tension showed that the increase in amplitude led to higher values.

The values of surface-tension as determined by several investigators using different methods are found to vary considerably among themselves, as is shown by the following graph (fig. 1). The curves *a*, *b*, *c*, *d* show the results as found by them.

It is noticed in these curves that the lowest values are given by the capillary-tube method, and the highest are those from the adhesion ring. Lord Rayleigh's values are intermediate between them.

The present work has been undertaken to find out whether the ripple method carefully conducted would lead to results in conformity with other methods.

## *2. The New Arrangement of the Ripple Method.*

(1) The present authors adopted the method of ripples, and in a note to 'Nature'\* described a device in which the stroboscopic effect was perfect inasmuch as a second fork was not necessary.

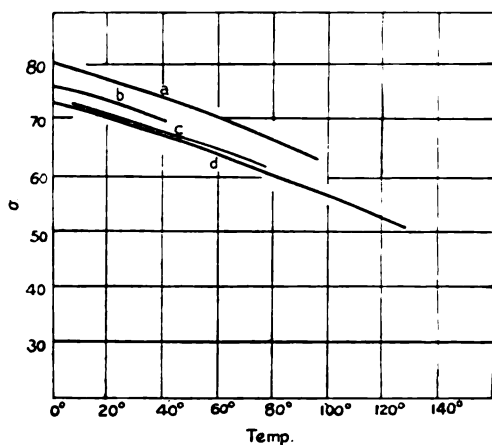
\* 'Nature,' xiv. (1925).



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- (2) Photographic records of the ripple forms were taken.
- (3) The frequency of the fork was determined with the help of a standardized seconds pendulum and a chronographic record.
- (4) The amplitude of the vibrating plate was kept within low limits.

Fig. 1.

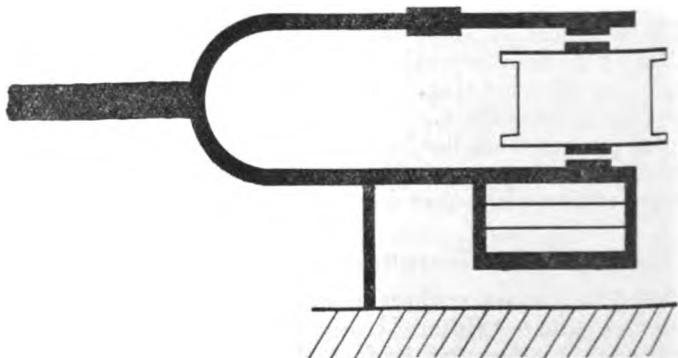


$a$  = Adhesion ring (Weinberg).     $c$  = Capillary tube (Weinstein).  
 $b$  = Hanging drops (Sentis).     $d$  = Capillary tube (Ramsay & Shields).

The method is described in detail as follows :—

To the lower prong of electrically-maintained tuning-fork frequency (about 100 d.v.), rigidly fixed to a heavy base, is

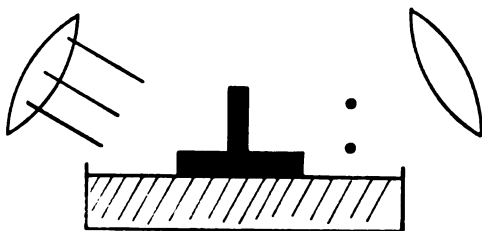
Fig. 2.



attached a rectangular framework of aluminium having two fine steel wires running horizontally along the length of the framework (fig. 2).

A horizontal metal blade three inches long attached to the same prong serves the purpose of a dipper to excite linear waves, on the surface of the water (fig. 3).

Fig. 3.



The plane of the viewer being at right angles to the dipper, the ripples travel across the viewer normal to its plane.

Divergent light from an arc lamp after being collected into a parallel bundle by a collimating lens is incident obliquely to the water-surface. A porcelain trough (10 in.  $\times$  6 in.  $\times$  1½ in.) contains the liquid, and a box with glass sides covers the whole arrangement to keep the liquid surface clean. The trough and all other accessories are placed on a solid masonry pillar separated from the main floor to avoid extraneous vibrations which cause modifications of the ripple forms. The reflected beam of light passing through the viewer is obstructed by the wires, and an observer looking down the direction of light finds a stationary wave-form of the ripple on the vibrating wires. A camera is used in photographing these patterns on a magnified scale. The plane of the incident beam being normal to the direction of propagation of the ripples, the light reflected from the crests and troughs can thus be sharply focussed on a plane placed at right angles to this direction, whereas the light from the shoulders of the waves will be reflected in different directions; the wires of the viewer will not obstruct these beams, and this part of the wire image will be absent in the stroboscopic image focussed on the photographic screen. Even with very low amplitudes the image will appear diffuse. The picture, which shows the form of the ripples distinctly, could thus be secured only when the axis of the photographic lens makes an angle with the direction of the reflected light from the undisturbed water-surface. Under this circumstance the phenomena are similar to the appearance of a surface examined by Foucault arrangement. The entire field appears as a dull background on which

the stroboscopic shadow of the wire is indicated as a dense black sinuous curve, which is the representation of the form of the ripple on the liquid surface. With some care in the adjustment of the direction of the axis of the lens, this wavy pattern can be made of uniform density through the entire length of the picture. With very low amplitudes, however, some difference in the density still remains in the different parts of the curve (Pl. XXI.).

Any very slight impurity on the surface of water which lowers the surface-tension shortens the wave-length, producing a sharper inclination of the shoulders of the waves, and the density of the crests and troughs gets more and more deepened; finally these portions only are visible. As suggested by Lord Rayleigh, the surface conditions have also been examined by observing the movements of camphor particles, and it has been found that the appearance of the form of the ripples on the screen is a clear indication of the nature of purity of the surface.

Another factor which modifies the form of the ripples is the size of the exciting blade. With the trough used the best size is three inches, and sizes smaller than that produce rounding of the edges of the linear ripples. This rounded character of the edges is easily seen by observing the surface with the help of a phonic wheel. Moreover, in this case the sinuous curve on the screen gets bent in the direction of the bends. With a bigger-sized blade the reflexions from the sides of the trough become very troublesome.

Another noticeable feature was the formation of streamer-like appearances from the surface of the exciter, which were very troublesome in the beginning. By auxiliary experiments it was found that the streamers were to a great extent due to (1) amplitude of the exciter, (2) the rigidity of fixing of the exciter, (3) the planeness and polish of the surface of the exciter in contact with the liquid, and (4) upon the nature of the material of which it was made. A dipper of glass was not found quite as satisfactory as one of brass. An exciter of pure silver with its surface optically worked and highly polished gave the best result; an aluminium exciter carefully made was fairly good, but its surface had to be taken out and repolished from time to time.

As the amplitude of the ripples modifies the values of the surface-tension, leading to higher values with increased amplitudes, some preliminary observations were made to determine the maximum amplitude that could be used. It was found that the relation between the amplitude and the wave-length should be kept in the ratio of 1 : 6 in order to get a concordant result. To reduce the amplitude of the

ripples, the exciter was fixed at some distance from the viewer and closer to the base of the fork.

The question of the depth of the liquid is another factor which must be paid attention to. As has been pointed out by Lord Rayleigh in his paper cited above, it follows an exponential law, and for wave-lengths up to 4 mm. the depth has been kept more than 2 cm., and in this case the depth factor is negligible.

### 3. *Measurement of $\lambda$ , $n$ , and Results.*

A thin metal plate with two fine notches at a measured distance is fixed to the electromagnet driving the fork, and is placed so as to be in the same plane as the wires of the viewer and in a line with them, and this plate is photographed along with the curves. This gives the magnification of the system. The wave-lengths are measured on a Hilger cross-slide micrometer fitted with a low-power microscope so as to avoid bringing in the field of view the grains of the photographic plate. The individual readings differed only in the third place of decimals for a centimetre, which was further corrected by taking a group of five at a time.

The frequency of the fork was determined with the help of a Cambridge chronographic recorder tuned in unison with the fork, along with the records from an electrically-maintained standard clock beating seconds. The clock is checked every day with the help of a chronometer. The records are examined with a low-power microscope, and a cross-hair in the eyepiece and a number of coincidences are noted, and the frequency could thus be determined correct to the second place of decimals.

Conductivity water prepared in the Physical Chemistry Department was used throughout the experiment, and its conductivity was determined before and after the experiment to find out any change due to the action of the exciter. It was found that, though the conductivity increases slightly after two hours, it is negligible in half-an-hour, which is the time taken for each set of experiments.

The final result is tabulated as follows:—

“ $g$ ” for Calcutta is taken as 978·815.

$t^{\circ}\text{C.}$	$\rho$ .	$\eta$ .	$\lambda$ in cm.	$\sigma$ dynes/cm.
18·5	0·9985	93·69	·381	72·81
29·4	0·9958	93·71	·378	71·68
35·6	0·9948	93·81	·374	70·25
47·5	0·9992	93·92	·371	68·42
56·2	0·9852	94·01	·367	65·89
64·1	0·9811	94·11	·366	64·53

The temperatures were determined with a normal thermometer certified by the Physikalische Technische Reichsanstalt.

#### 4. *Summary and Conclusions.*

1. A new stroboscopic arrangement has been devised for the determination of surface-tension of liquids by the method of ripples.

2. A new method of observing and photographing the form of the ripples has been devised. With the help of this arrangement a more accurate measurement of the wavelength of the ripples has been rendered possible.

3. The results that have been arrived at are fairly in agreement with the values of Weinstein and Volkmann, who used the capillary-tube method, but are lower than the values found by other workers using different methods.

Experiments are in progress to determine the surface-tension of different liquids at different temperatures, and also ripples of different frequencies.

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#### CXII. *On Surface-Tension of Solids.*

By G. N. ANTONOFF, *D.Sc. (Manch.)*\*.

IT appears at first sight that the surface-tension of a solid can be determined by measuring the breaking stress of a crystal. If the molecular structure of the substance is known, there are all the necessary data to calculate the surface-tension of a solid.

I tried to use the above method in order to find out the surface-tension of rock-salt, and found a value 1.4 dynes per cm., instead of 3000–4000 dynes per cm. as I expected from elementary theoretical considerations.

However, a crystal is never perfect, and apparently always contains some minute cracks; there is always some doubt as to whether an experiment as above gives the desired information, although the breaking stress is as a rule a very definite figure varying within only a very narrow limit.

For this reason it is desirable to devise a method of measuring the field of force exercised by molecules in some other way. Before describing a method of this kind I must say a few words about surface-tension generally.

\* Communicated by the Author.

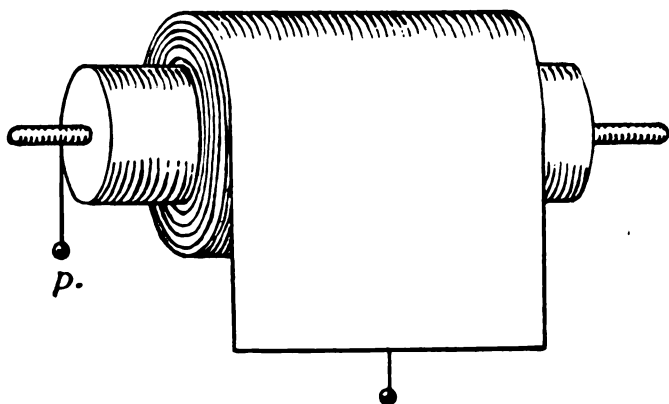
## DEFINITION OF SURFACE-TENSION.

The surface properties of liquids are such, as if the liquid mass was enclosed in a kind of membrane tending to contract under the effect of molecular forces. Some authors speak of it as of an elastic membrane, in the sense that it contracts and expands under the effect of external forces.

However, the surface properties of liquids do not altogether justify the above analogy. The elastic body expands proportionally to the force applied, whereas the liquid membranes expand in such a way that the acting force remains constant.

I can therefore propose the following mechanical model, which reproduces more accurately the characteristics of a liquid. Imagine a kind of roller blind (see fig. 1) with an

Fig. 1.



ideal membrane, *i. e.* whose thickness and weight = 0, and which moves without friction, (In this sense the drawing is not strictly correct, as it shows an appreciable thickness of the membrane.) If force is applied to the curtain, it will begin to unroll as soon as the applied force reaches a value slightly exceeding the force  $p$ , acting in the opposite direction.

Let  $l$  be the width of the membrane, and  $\alpha$  the pull per unit width ; then

$$2l\alpha = p,$$

where  $p$  is the weight necessary and sufficient to produce stretching of the membrane.

It is seen that the expression for the work done in producing a unit surface is practically the same, viz.

$$pdx = 2\alpha dx,$$

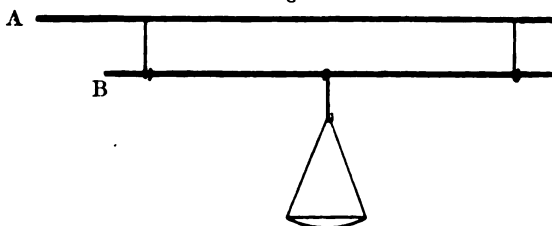
$$\int_0^h p dx = ph = \int_0^h 2\alpha dx = 2\alpha h,$$

where  $h$  is the vertical dimension of the film produced.

$$\therefore \alpha = \frac{P}{2l}.$$

Thus the surface-tension defined as work is numerically equal to the same defined as force per unit width. (If the force  $p$  is not constant, as is the case in elastic bodies, the above expression cannot be integrated in the above way, and the expression for work is not identical with the expression for force.)

Fig. 2.



The above model can be reproduced in the following experimental device.

Imagine a thin rod A fixed horizontally (see fig. 2). If another rod B is placed in close contact with A, and they are both moistened with a liquid, they will adhere to one another. A certain definite weight must be applied to B in order to detach it from A, whereby a film of liquid will be produced between A and B.

Practically, in most cases, the formation of the film results in the breaking of the same. Thus, experimentally, the weight producing the breakage of the film is used for determination of surface-tension.

Such a method is very instructive as illustrating the surface-tension in a direct way, but it is seldom used and some other methods are generally preferred as more accurate. One of the drawbacks of this method is that the film always evaporates, and it is therefore not very suitable for working at different, and especially elevated, temperatures.

I describe this method somewhat in detail, because I shall soon make use of it under suitable conditions when it can render invaluable service.

## SURFACE-TENSION OF SOLIDS.

In certain cases one can devise a method of measuring the surface-tension of a solid, and it can be done on the following theory.

If a liquid rises in a capillary tube, it means that the cohesion between the particles of glass (or other material of which the capillary is made) and the liquid is greater than that between the particles of liquid.

If the surface-tension of the liquid is greater than that of the solid it is in contact with (as in the case of mercury-glass) the reverse takes place, *i. e.*, the liquid not only does not rise in the capillary, but there is a capillary depression, which is a measure of surface-tension just in the same way as capillary rise was a measure of it in the previous case.

Therefore it is necessary to find such systems whose surface-tension can be varied within the desired limits, in order to reverse the capillary action in a tube of material whose surface-tension is to be measured.

Thus, I took a capillary tube coated with paraffin inside. By placing it in water one can observe a marked capillary depression. On the other hand, I took a certain solution of isobutyric acid, whose surface-tension was known to me. This solution produced a definite rise in the same capillary.

By varying concentration of isobutyric acid one can notice that one intermediate concentration will produce neither capillary rise nor depression. The meniscus inside the capillary will remain on the same level as outside it.

This will happen just when the solution used has the same surface-tension as the material of the capillary.

As it is not easy to find this solution exactly, I experimented with several concentrations on either side of the point at which the capillary action is reversed, and determined the point by interpolation.

I thus found figures for paraffin and beeswax which are somewhat higher than the corresponding values found for these substances by the capillary method in the liquid state just above their melting-point.

These figures are quite reproducible, if the experiment is repeated with fresh material. But on standing there is always observed a marked change, *i. e.*, the liquid begins to wet paraffin as a result of a prolonged action, the capillary depression gradually diminishes and may change into capillary rise. This is either due to a kind of polarization produced in the solid by contact with liquid, or it may be a chemical action of some kind. Anyway, judging by the fact that figures obtained at first are of the order expected



from capillary determination of these substances above their melting-point, I believe these figures are characteristic, and not the ones observed as a result of prolonged action.

I shall give a few figures obtained by the above method for beeswax and paraffin.

#### *Beeswax.*

16 per cent. isobutyric acid (its surface-tension  $\alpha$  = about 26 dynes per cm.) gave a rise in a capillary tube coated with beeswax of about 3 mm.

Pure water ( $\alpha$  = 72 dynes per cm.) gave a depression of about 4 mm.

The transition point, i. e., the point at which there is no capillary rise or depression at all, corresponds to the concentration of acid about 9 per cent., having  $\alpha$  = 46 dynes per cm.

Another experiment with a different capillary gave :

16 per cent. solution ..... 8 mm. rise.

Water ..... 6 mm. depression.

Transition point at 9 per cent. of acid,

thus the surface-tension of beeswax = 46 dynes per cm.

#### *Paraffin.*

16 per cent. solution of isobutyric acid . 6 mm. rise.

Water ..... 12 mm. depression.

Transition point at 10.7 per cent. of acid for which

$\alpha$  = 41 dynes per cm.

Another experiment with fresh coating gave the same figure with acid and 13 mm. depression with water, which gives a slightly lower figure for  $\alpha$ , viz.  $\alpha$  = 40.4 dynes per cm.

So with fresh surfaces the experiment repeats itself fairly well, but on standing all values begin to change.

The limitations of this method are due to the chemical or dissolving action, which can always intervene and make the experiment impossible. But the other difficulty is to find systems whose surface-tension can vary within the desired ranges to suit the given solids.

#### THE SURFACE-TENSION OF GLASS AND ROCK SALT.

It is often assumed that glass is not a solid but rather a viscous liquid. Its tensile strength may vary within wide limits according to the conditions in which it was kept on cooling, and there is apparently an inevitable tendency to

form minute cracks which is responsible for a very low tensile strength generally observed experimentally.

However, all that is of no importance from the point of view of the method I am going to use to determine the surface-tension of glass. The fact is that glass does not change its shape during the experiment, and in this sense is like a solid. For measuring the surface-tension of glass I took advantage of the following facts.

Among the existing liquids we cannot easily find any suitable substances or mixtures of substances giving us values of surface-tension between 70 dynes per cm. (surface-tension of water) and 500 dynes per cm. (surface-tension of mercury).

Now I have come across certain substances of the nature of semi-fluids, which are capable of forming films of very high surface-tension. I can thus produce a system whose surface-tension may be varied at will within such limits as to cover the gap between the above figures.

To this end I have made the following experiments.

I acquired on the market two powdery substances, one being substantially lamp-black, and the other a blue pigment consisting substantially of ultramarine. Then I found that on mixing the above with some stable and non-volatile liquid, a paste can be obtained whose surface-tension can be measured by the method described on p. 1260.

Among the powdery substances I tried for the above purpose, there were bodies of a distinctly different nature, and only some of them were suitable for the purpose. I am not able yet to tell what this difference was due to, but it is quite real and can be shown in the following way.

I mix the lamp-black with some liquid, for example, salad oil—which is not volatile and is capable of forming pastes stable for many months.

The surface-tension of such paste can vary within wide limits, beginning from 3.5 dynes per cm. (surface-tension of pure salad oil), according to the proportion of the ingredients and their state of sub-division.

On the other hand the blue pigment, no matter how intimately mixed with oil, will always have a somewhat different appearance. It will not be as shiny as the other while being mixed. After mixing is finished, the impression is, as if oil comes out on the surface and forms a thin film. Measurements of surface-tension of this paste reveal a substantial difference as compared with the previous case. The figures obtained with the apparatus on p. 1260 do not show constancy. They differ little from those for pure oil,

and on standing generally give a figure identical with that of pure oil. I thought at first that this substance wanted a more intimate mixing and more prolonged grinding, but I found that it does not make any difference whatever. I do not know, as I have said, what this difference is due to, but substances of this kind are of no interest to me from the point of view of the object of this paper.

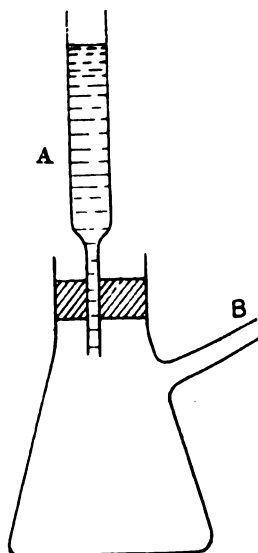
The paste formed by mixing the lamp-black with salad oil (or other suitable liquids), however, happened to be most suitable for measuring the surface-tension of glass and some other substances.

The actual experiment was done as follows.

Pastes of different concentrations were prepared and their surface-tensions measured by the apparatus of fig. 2.

The samples of the above paste are placed in tube A shown in fig. 3. This tube is joined to a thin capillary

Fig. 3.



and a suction applied at B. If the resistance in the capillary is sufficiently high, the paste slowly moves in the tube A downwards until the whole content of the tube A is driven into the flask.

By placing pastes of different concentrations into A one can observe the following :—

Sometimes the tube A on being emptied remains coated

with a thin film of the paste. In some other cases the paste does not adhere to the glass and descends as a result of suction, leaving behind a perfectly clean and transparent glass surface.

It can be seen that the pastes with low surface-tension generally wet the glass.

But when the surface-tension of the paste reaches a certain value, the paste ceases to wet the glass.

The experiment with pastes made of different substances and different liquids revealed always the same figure, viz. about 130 dynes per cm. for a given glass.

In another series of experiments with glass of a distinctly different chemical composition, I obtained a somewhat lower figure, but constant within narrow limits.

I assume that the paste wets the glass so long as its surface-tension is less than that of glass, and conversely, the surface-film does not adhere to the glass if the former has a higher surface-tension than the glass. The surface-tension of the paste at the transition point is therefore equal to the surface-tension of the glass.

*Thus the figure 130 dynes per cm. is the value of surface-tension of glass, which does not depend upon such things as cracks in its surface, and is based on the measurement of the actual field of force exercised by the surface of glass. The figure obtained is of the order expected for a substance of the nature of fused salt.*

In the experiment with paraffin there was observed a change in physical properties according to the duration of contact between the solid and the liquid.

It may be due to a kind of polarization, or dissolving action which, of course, would tend to upset the value of surface-tension thus obtained.

In the case of the above pastes in contact with glass no such changes were noticed by myself. Apparently the glass is not soluble in oil or its pastes, and I therefore believe that the above figure may be an accurate value of the surface-tension of glass.

The method is somewhat tedious, and it requires a lot of patience in order to find the transition point more accurately. In the case of paraffin it was possible to find the transition point by interpolation. In this case it is necessary to spend a lot of time in gradually approaching it from both sides.

In a similar manner I measured the *surface-tension of rock-salt and found it, as an average of several experiments, about 315 dynes per cm.* As these experiments present certain

*Phil. Mag. S. 7. Vol. 1. No. 6. June 1926. 4 M*

difficulties, especially in case of rock-salt, I shall describe the actual experimental conditions more in detail, but I shall do so in a subsequent paper.

#### CONCLUSION.

In this paper I describe a method I devised for measuring the surface-tension of solids.

The method is not universal, but it can be used within a fairly wide range of values of surface-tension, provided no other factors intervene (such as solubility or other forms of action). I came to the conclusion that this method is suitable for measuring the surface-tension of mineral salts, which presents interest from the point of view of structure of crystalline matter as revealed by the X-ray method. I thus obtained certain values for glass and rock-salt.

The question may arise whether they actually represent the values of surface-tension, or whether they may be constants somewhat related to it. I have fully considered this point, but, taking into account the elementary theory, I do not think the constants can be anything else. However, I am going to discuss this point once again in a subsequent paper in which I shall describe in detail the actual experimental conditions.

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London, W.C. 1.

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#### CXIII. *The Conductivity of Clouds dispersed from an Arc.* By H. P. WALMSLEY, M.Sc.\*

WHEN an electric arc is produced between metallic electrodes in air, a cloud of fine particles is dispersed. In the case of easily oxidisable metals, such as cadmium, lead, copper, aluminium, and zinc, the particles consist of oxides; but platinum, silver, and gold yield metallic particles. Some of the particles are visible in the ultramicroscope and show marked Brownian movement. Hitherto, they have been of interest mainly in connexion with the quantitative study of Brownian motion and the validity of Einstein's formula for the displacement. By direct observation with the ultramicroscope, De Broglie<sup>(1)</sup> found for particles from arcs in which zinc, platinum, and silver electrodes were used, that some were charged positively, some negatively.

\* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

and others were neutral. Ehrenhaft and others have employed the charged particles in determinations of the charge carried by the electron. Most of the clouds produced by dispersal processes contain charged particles. De Broglie<sup>(2)</sup> has used particles in tobacco smoke, and from determinations of the mobility and the displacement produced by the Brownian movement, he obtained a value of  $4.5 \times 10^{-10}$  e.s.u. for  $e$  their charge. It thus appears that the charged particles usually carry the electronic charge, although for some of the larger particles De Broglie obtained larger values of  $e$  and concluded that such particles carried multiple charges. The presence of charged particles should give conductivity to the cloud, and the experiments of McClelland<sup>(3)</sup> on an arc between platinum electrodes show that this is the case. McClelland maintained an arc between the electrodes and passed a constant flow of gas past it into an ionization chamber, consisting of a cylindrical brass tube carrying two electrodes. He was able to measure the conductivity in different gases and under varied conditions and determine the mobility of the ions present. Since his paper was published, Ehrenhaft<sup>(4)</sup> found that the clouds produce coarse condensates, which settle out on the walls of the containing-vessel, and concluded that the particles first produced by the arc—the primary particles—coagulated as the cloud aged. Whytlaw-Gray<sup>(5)</sup> and others confirmed this by following the process quantitatively. If the charged particles of the cloud are liable to increase in mass by coagulation as the cloud ages, one would expect to find decreases in mobility and to find ions of different mobilities co-existing, even if the initial ions were all similar. McClelland<sup>(3)</sup> showed, in fact, that the mobility of the ions from platinum decreased as the distance between the arc and the electrodes was increased, other conditions remaining constant. It is clear, however, that by using his method, the process can be followed only over a short stage in the life of a cloud. The present experiments were undertaken to follow the process over a more extended period.

### *The Apparatus.*

The experiments to be described were made on the clouds produced from an arc between cadmium electrodes. Cadmium was selected mainly on account of the ease with which it produces a cloud. The method of dispersal was identical with that described in detail by Professor Whytlaw-Gray<sup>(5)</sup>.

The cloud chamber consisted of a closed galvanized iron

tank of about 850 litres capacity which was earthed. Two rectangular holes about a foot square were cut in opposite sides of the tank and were closed with  $\frac{3}{4}$  inch plate glass to act as windows. The glass was held in a metal frame carrying lugs, which slipped over bolts fixed in the side of the tank and were secured by nuts. Rubber seatings were inserted between the glass and the frame and between the glass and the side of the tank which prevented fracture of the glass as the frame was bolted up and made the chamber air-tight. The chamber was filled with dry air free from dust and carbon dioxide, and was open to the outside air through a side-tube containing a cotton-wool filter and small sticks of caustic soda.

The cloud was dispersed by passing a direct current of 3 to 5 amperes between the cadmium electrodes for a few seconds and maintaining a draught across the arc by means of an electrically-driven fan. A steady stream of cloud was then drawn from the centre of the chamber through an ionization chamber and a flow-meter by means of a constant head aspirator. The ionization chamber consisted of a brass cylinder about 30 cm. long with a coaxial electrode protected in the usual way by a guard-ring. The electric field was applied by connecting the outer cylinder to one terminal of a battery of small accumulators, the other end of which was earthed. The current passing through the central electrode was measured by the rate of charging up of a Dolezalek electrometer, which was used at a sensitivity of 500–600 scale-divisions per volt.

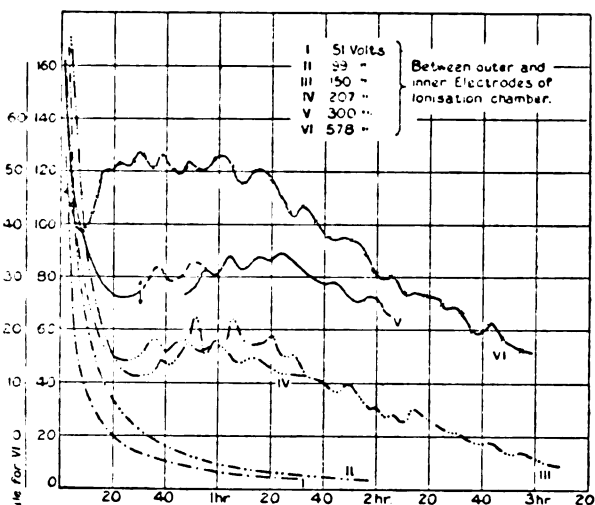
#### *The Effect of Field Strength on the Ionization Currents.*

Measurements of the ionization current were commenced as soon as possible after the production of the cloud and were continued until the current became negligibly small. The ionization curves therefore show the variation of the current with the age of the cloud. Ionization curves for clouds produced under approximately the same conditions were obtained with a series of different voltages on the ionization chamber. Some of these are reproduced in fig. 1. The currents are expressed in arbitrary units—scale-divisions per minute. The origin of time is taken at the commencement of sparking.

The group of curves shows several general characteristics, the most pronounced perhaps being the rapid fall in the current obtained during the first half-hour of the life of the cloud. All except two of the curves subsequently show

a tendency to rise, and when this happens the ionization curves become oscillatory. Oscillatory curves are not a

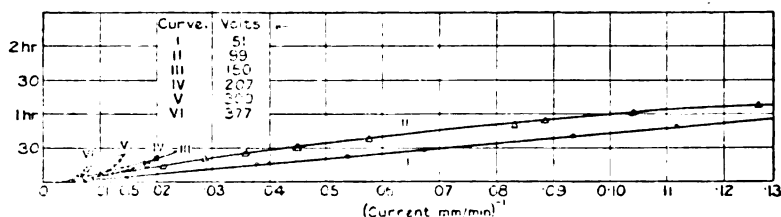
Fig. 1.



specific property of the clouds from cadmium. They have been obtained with clouds from zinc, aluminium, and arsenic, and are probably a general feature of oxide clouds dispersed in air.

Fig. 2 shows the curves obtained by plotting the reciprocals

Fig. 2.



of the current against age, for those portions of the curves which show the rapid fall. One of these is a perfectly straight line, one slightly convex to the axis of time, and the rest are concave to this axis. Since both positive and negative charges are present and rapidly disappear, there is a general agreement in these clouds with the law of recombination which holds for ions from Röntgen radiation. A



complete discussion of these curves is impossible without a knowledge of the source of the charges and the relative number of positive charges to negative. No experiments have yet been carried out on these questions, but indirect evidence has been obtained that the number of positive and negative charges are roughly equal for the cadmium oxide clouds. If we make the assumption that the positives are emitted by the hot metal electrodes and the negatives from the crust of oxide which is invariably produced on the electrodes by sparking, absolute equality in number is not to be expected. The effect of this inequality on the curves can be obtained as follows.

If  $n_1$  and  $n_2$  be the number of positive and negative ions per c.c. of the cloud, the law of recombination of ions, in the absence of any ionizing sources, gives

$$\frac{dn_1}{dt} = -\alpha n_1 n_2 = \frac{dn_2}{dt}, \quad \dots \quad (1)$$

whence

$$n_2 - n_1 = c \text{ (a constant)}. \quad \dots \quad (2)$$

So long as recombination only is operative, the difference between the number of ions of opposite signs remains constant, so the total charge per c.c. of cloud should remain unaltered with time. Assuming  $c$  positive, the preceding equation becomes

$$\frac{dn_1}{dt} = -\alpha n_1 (n_1 + c),$$

the solution of which is

$$\frac{n_1}{n_1 + c} = e^{-\alpha c(t-a)} = \frac{N_1}{N_2} e^{-\alpha c t}, \quad \dots \quad (3)$$

where  $a$  is a constant and  $N_1$  and  $N_2$  the number of positive and negative ions when  $t=0$ . Thus the ratio  $n_1/n_2$  of the number of ions decreases exponentially with time. The recombination increases with  $c$ , which is to be expected, since the number of collisions favourable to recombination of the positive ions must increase with increasing numbers of negative ions. If  $N_2$  is extremely great compared with  $N_1$ , the equation tends to the limiting form

$$n = N_1 e^{-\alpha N_2 t}.$$

This condition is approximately realized in the recombination of positively charged radioactive ions surrounded by the large number of ions produced by their radiations<sup>(6)</sup>.

If we expand the exponential term, we can transform (3) into

$$\frac{1}{n_1} - \frac{1}{N_1} = \frac{N_2}{N_1} \alpha t + \frac{N_2}{N_1} e \left( \frac{\alpha^2 t^2}{2!} + \frac{\alpha^3 t^3}{3!} + \dots \right). \quad (4)$$

If  $N_1 = N_2$ , this reduces to the form

$$\frac{1}{n} - \frac{1}{N_1} = \alpha t. \quad (5)$$

If  $N_1$  is unequal to  $N_2$ , this equation holds for small values of  $\alpha t$  provided we replace  $\alpha$  by  $\frac{N_2}{N_1} \alpha$ . Thus, if we plot reciprocals of the number of ions as ordinates and time as abscissæ, we obtain in the case of  $N_1 = N_2$  a straight line of slope  $\alpha$  and in the case of  $N_1$  unequal to  $N_2$ , a curve convex to the axis of time, whose initial slope is  $N_2/N_1$  times greater.

Returning to fig. 2, it is seen that the majority of the curves are concave to the axis of time, *i. e.*, that the charges disappear slower than the law of recombination in (1). The only remaining factor, in the absence of ionizing sources, influencing the rate of recombination is  $\alpha$ , hence for these curves it is necessary that  $\alpha$  decrease with time. It follows that in this stage of the cloud, either the collision frequency decreases or the fraction of collisions entailing disappearance of the cloud diminishes. If the Brownian motion of the ions obeys Einstein's displacement formula, the former assumption necessitates the mass of the ions increasing with time, either by coagulation or adsorption of matter from the medium. The second possibility might be realized if the particles adsorbed an insulating gas. Both effects may occur in the clouds.

Most of the clouds from cadmium electrodes give a reciprocal curve concave to the axis of time. With aluminium, however, at least half of the curves obtained are convex. The rate of disappearance of the charges in the first half-hour indicates that with the majority of clouds from cadmium, one at least of the following effects must occur:—

- (a) There is a gradual increase in the mass of the ions as the cloud ages.
- (b) The ratio of the number of collisions which result in recombination to the total number of collisions decreases with time.
- (c) There is a production of ions in the cloud as it ages.

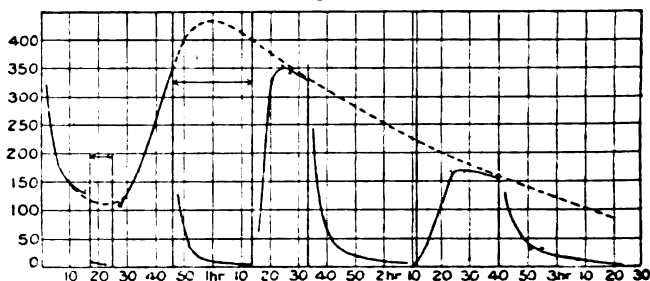
The direct measurements of mobility made by McClelland show that the mass of the ions from a platinum arc increases as the ions age.

*Ionization Changes in Intense Electric Fields.*

From fig. 1 the type of ionization-time curve is seen to depend largely on the electric field in the ionization vessel. With moderate to high fields, the ionization in this type of curve falls to a minimum at about half an hour and then rises to a maximum, which is followed by a slow fall. The increase in current persists at times for as long as three hours. Fig. 3 gives a more typical curve than any in fig. 1. In all cases the rise after the minimum is not a smooth curve but shows oscillations in the ionization. The weaker fields do not, in general, show this rise in current. We are, therefore, led to associate the rise with ions of low mobility, such as would pass practically uninfluenced through the weaker fields.

The ionization currents are a measure of the charge driven

Fig. 3.



by the field to the electrometer. Hence, before we can interpret the measurements in terms of the changes in the cloud, we must clearly distinguish between the changes in the ionization current, which are due to the action of the field, and changes which are due to ions in the cloud. If a number of ions are distributed initially throughout a volume  $V_0$  and move under the influence of forces arising from external charges on electrodes of any shape, it is easy to show<sup>(7)</sup> that the motion is such that at any subsequent time all the ions are contained in a volume equal to  $V_0$ . Thus the electric field only changes the direction of motion of the ions, so that if a steady state is attained and  $n$  ions of like sign enter the field in unit time, the number of ions collected by the electrode is  $n$  and is independent of their mobility. Under these circumstances the changes in the ionization current are a measure of the changes in the ionization of the cloud

If, however, from some cause the mobility of the ions changed, their velocity in the electric field would alter. In the steady state the number received by the electrode per unit time will still be  $n$ , but the number of ions in motion in the field will change inversely as their velocity. The rearrangement of the ions within the electric field will cause additional ions to be driven to the electrode and will produce a temporary rise in the current through the electrode: or, it will abstract ions from the incoming flow and produce a temporary decrease in the current through the electrode. Such changes in the ionization current may be considered as due to the action of the electric field. Temporarily we will neglect effects of this nature and assume that the currents measured are proportional to the ionization in the cloud.

Returning to fig. 3, it is clear, with this assumption, that there is a production of ions in the cloud subsequent to the first half-hour, and we have just seen that the new ions are ions of low mobility. The only obvious external agency producing ions within the cloud is the penetrating radiation of the earth. If  $n_s$  be the number of ions in the steady state when the number  $q$  produced per second by the radiation is equal to the number recombining per second, we have

$$n_s = \sqrt{\frac{q}{\alpha}},$$

so that the saturation current due to natural ionization of a cloud of ions in the steady state increases very rapidly with decrease in mobility. The number of ions produced by the radiation increases with time according to the formula (if  $n=0$  for  $t=0$ )

$$n = n_s \tanh \sqrt{q\alpha} t.$$

The cloud will be approximately in the steady state when  $t$  is large compared with  $1/2 \sqrt{q\alpha}$ , so that a considerable time may be necessary for the ionization to rise to a maximum. As  $\sqrt{q\alpha}$  increases,  $n$ , which is proportional to the ionization current, approximates more and more rapidly to the value  $\sqrt{q/\alpha}$ . If  $q$  be constant, as will be the case if the ions in the cloud are produced by the penetrating radiation of the earth, the coefficient  $\alpha$  must pass through a minimum and then increase, since the ionization current in fig. 3 passes through a maximum. This is highly probable, for the value of  $\alpha$  determined in this way is an average value, so that it is only necessary for the heavier particles in the cloud to fall

out preferentially by precipitation under gravity, to account for the effect.

Ionization produced by the earth's penetrating radiation, however, does not appear sufficient to account for the magnitudes of the currents measured\*. Hence there must be some other source producing ions. For these  $\sqrt{q/\alpha}$  passes through a maximum and finally practically vanishes. Since the ions are of low mobility, it is quite unlikely that the maximum value which  $\alpha$  can attain will be greater than 3400, its value for normal ions produced in air by, say, Röntgen radiation. Thus  $q$  must eventually decrease with time and vanish; and, whatever changes  $\alpha$  undergoes, the rate of production  $q$  of new ions in the cloud first increases to a maximum and ultimately decreases to zero.

\* The number of ions per c.c. and their rate of production,  $q$ , on this hypothesis can be estimated as follows. The currents for curves 3, 4, and 6 of fig. 1, which are some of the weakest measured, rise to a maximum of between 50 and 60 scale-divisions per minute, corresponding to a rate of charging-up of the electrometer of about  $\frac{1}{5}$  volt per minute. Taking the capacity as 60 cm., the current  $i = 3.2 \times 10^{-4}$  E.S.U. If each ion carries unit charge the number of ions collected per second is  $3.2 \times 10^{-4} / 4.8 \times 10^{-10} = 6.6 \times 10^5$ . The rate of flow of cloud through the ionization chamber was 4 c.c. per second, so that the number of ions per c.c. of the cloud is of the order of  $1.6 \times 10^5$ . This is about one-tenth of the number of ultramicroscopical particles counted in similar clouds of the same age by Whytlaw-Gray<sup>(3)</sup>.

If the ions arise from a source producing them at a rate  $q$  per second, the number of ions per c.c. of the gas increases with time according to the equation

$$n = \sqrt{\frac{q}{\alpha}} \tanh \sqrt{q\alpha} \cdot t.$$

Thus  $n$  is equal to 98 per cent. of its equilibrium value  $\sqrt{q/\alpha}$  when  $t' = 2.3/\sqrt{q\alpha}$ . In curve 6 of fig. 1, the time required is not likely to be greater than 20 mins., which makes  $\sqrt{q\alpha} = \frac{2.3}{1.2} \times 10^{-3}$ . But we have

seen that  $\sqrt{\frac{q}{\alpha}} = 1.6 \times 10^5$  so  $q = 3.2 \times 10^2$ . Since  $q$  varies inversely as  $t'$ , the precise value taken for  $t'$  makes little difference as regards the order of magnitude of  $q$ . Hence for the cloud in question, the ionizing source would have to supply at least 300 ions per c.c. per second to account for the effect. This is a hundredfold greater than the rate of production due to the earth's penetrating radiation. With denser clouds, there is no difficulty in obtaining currents at the maximum, a hundred times greater than in the example quoted, which suggests that the ionization must arise from processes occurring within the cloud.

*Mobility Changes in the Cloud.*

The preceding observations seem to indicate that the time of minimum ionization divides the electrical history of the clouds into two distinct parts. For convenience we will refer to the parts as the early stages and the later stages of the cloud. The reciprocal curves (fig. 2) show that in the early stages the changes in mobility of the particles are relatively gradual. The changes in the later stages will be found to be more marked, and can be described best by reference to a particular experiment (fig. 3). The field employed (400 volts on the ionization vessel) was sufficient with the rate of flow employed to give the saturation current for all ions of mobility greater than  $1 \times 10^{-4}$  cm./sec./volt/cm. Although ions of less mobility would not give a saturation current, yet these if present would contribute something to the current measured. The field, therefore, was sufficiently intense to deal with a number of particles of fairly low mobility.

From fig. 3 the ionization in the early stages is seen to drop rapidly to a minimum. The subsequent rise reaches a maximum and then falls away, the general course of the cloud being indicated by the dotted line. The vertical lines are drawn in pairs. At the time corresponding to the first line of a pair, the flow of cloud through the ionization chamber was stopped, and observations of the current due to the ions within the chamber continued. When this current died away, the flow of cloud was recommenced at the time indicated by the second line of the pair.

When the flow of cloud is steady, there is a distribution of ions in motion within the electric field, extending from one electrode to the other. Stopping the flow of cloud cuts off the supply of ions to the electric field, so that the subsequent current is due to the withdrawal of the ions which were between the electrodes at that moment. The curves in fig. 3 show that the times  $T$  required for the field to discharge these ions increase as the cloud ages. If we assume that there is no production of ions within the field, the time  $T$  is obviously the time required for the slowest moving ion within the gas to cross the electric field. In these experiments, unless  $T$  is greater than about 2 minutes (corresponding approximately to a mobility  $k = 2.78 \times 10^{-5}$ ), there is little chance of detecting this current at all; so the ions whose charges produce it must have mobilities which require at least two minutes to cross the field and are therefore large ions. Further, since  $T$  increases with the age of

the cloud, the mobility of the slowest moving ions in the cloud gradually decreases as the cloud ages.

The two rise curves which are taken after the time of maximum ionization conform with this view. The ionization current measured by the electrometer after recommencing the flow of cloud, will only attain a value proportional to the number of charges per unit volume of the cloud after a time  $T'$ , which is, as before, determined by the time taken for the slowest moving class of ions in the cloud to cross the electric field. It is seen that the later curve requires a longer period to attain its maximum than the former, so that the largest type of ion present in the later one has considerably slower mobility than the slowest moving ions present at the earlier period of the cloud. The rise curve occurring before the time of maximum current would be expected on these grounds to rise still more rapidly, but it must be remembered that the effect here is masked to a certain extent by the disappearance of the small ions from the cloud.

We have yet to consider the effect on the curves of the production of ions, which has been shown to occur in the cloud. Since the effect of the electric field on the ions is merely to change their motion, it is clear that a production of similar ions at a point travelling with the ions will not alter the effect. If the field is sufficiently intense to produce saturation for ions of any mobility, a production of ions within the cloud will be indicated by a corresponding rise in the ionization current. Thus on recommencing the flow of cloud to the electric field, the time required for the current to attain its final value is independent of any production of charges within the cloud and is determined, as before, solely by the time required for the slowest moving ions present to cross the field. The two rise curves occurring after the maximum, therefore, still indicate the decrease in mobility of the slowest moving ions in the cloud at those times.

We have already shown that the rate of production of ions in the cloud passes through a maximum, and this is independent of assumptions as to what occurs to the coefficient of recombination  $\alpha$  and consequently to the average value of the mobility of ions. We can therefore select pairs of times at either side of the maximum at which the rate of production  $q$  of ions in the cloud is the same for each pair. As the extreme case, we will assume that the fall curves are due entirely to ions which are produced from the cloud which is left within the ionization chamber when

the flow is stopped. For each pair the field removes all the ions from the cloud quicker at the earlier time than at the later time. Thus the ions produced at the earlier period must be more mobile than those produced later : so the fall curves show that the average mobility of the cloud decreases as it ages. The rise curves have shown that the mobility of the slowest moving ions decreases as the cloud ages, so both effects must take place concurrently. The effects due to ions in motion in the field when the flow of cloud is stopped conform with the effects due to the new ions produced in the field.

Returning to the experimental curve, it will be seen that after 20 minutes in the life of the cloud, the large ions do not contribute more than 10 per cent. and possibly not more than 5 per cent. of the total current obtained from the cloud at that time, whilst earlier the percentage is less. Thus as the cloud ages the number of large ions increases from a very small quantity to a maximum and then slowly decreases. The rate of production of new charges, therefore, is roughly proportional to the number of large ions in the cloud, and not to the number of small ions such as are responsible for the currents in the early stage of the life of the cloud. When new charges are produced in the cloud they appear mainly as large ions.

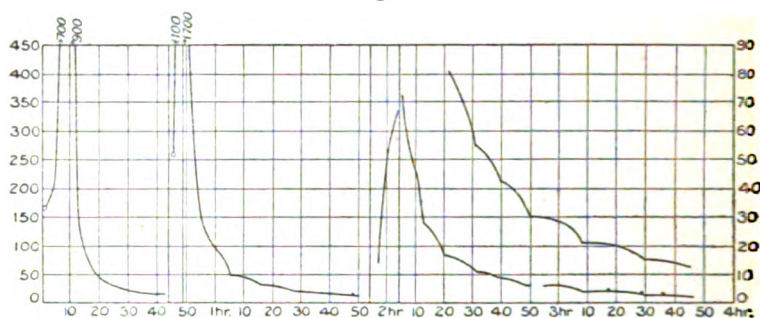
#### *Variations with Mass of Material Dispersed.*

The mass of material dispersed by the arc is obviously some function of the time of sparking and the current. By increasing either we obtain changes in the cloud. If we increase the amount of material dispersed, the mobility of the ions in the early stages, as judged by their rate of recombination, decreases. To compensate for the diminished mobility we can increase the field in the ionization chamber, as otherwise the currents become too feeble for measurement. With such clouds we may nearly eliminate the initial fall (Curve VI, fig. 1), or we may even obtain an ionization curve which commences to *rise* with time (fig. 4). The initial rise may be due to two causes. The ionization curve will rise with time provided the mobilities of the ions produced initially are sufficiently low. They will then require a long time to cross the electric field, and a corresponding time must elapse before the current becomes proportional to the volume density of charge within the cloud. But if the rate of production of new ions in the cloud, which gives rise to the minimum in fig. 3, is greatly increased, the



time at which it occurs will decrease. In consequence, a sufficiently great rate of production will tend to make the minimum disappear altogether and the ionization current will commence to rise with time. Such a curve, treated in the same manner as fig. 3, is shown in fig. 4. The field here removes all charged particles of mobility greater than  $5 \times 10^{-5}$  cm./sec./volt/cm.—the mobility of a spherical particle of radius  $1.1 \times 10^{-5}$  cm. which carries one electron and obeys the Stokes-Cunningham law. The last two rise curves show an increase in the size of the ions, since the slope of the former is more steep than the latter. The three fall curves disappear at diminishing rates. The last one is redrawn with ordinates magnified five times. Again, the rise of the initial curve, which, if due to the presence of large ions only, should be more rapid than the second, is

Fig. 4.



modified by the disappearance of ions due to recombination and by the growth of the large ions.

If there were no production of new ions in the cloud, the last fall curve would indicate that the large ions are present in groups. Suppose we had groups of ions present of gradually diminishing mobilities  $k_1, k_2, \dots$ . The times for these to cross the electric field are  $T_1, T_2, \dots$ . If now we fill the ionization chamber with a mixture of these types, and at time  $t=0$  apply a field, the ions will move towards the electrodes giving a steady current until  $t=T_1$ . At this stage all ions of mobility  $k_1$  will have been removed and the current will then drop and remain constant until  $t=T_2$  and so on. We thus obtain a stepped curve. Diffusion of the particles and self-repulsion due to their charges whilst they are in motion in the field, will prevent the density changes at  $T_1, T_2$  becoming abrupt, and will tend to smooth out the steps, making them concave to the time axis, which

is the shape of the last fall curve in fig. 3. The production of ions in the field during the decay of current complicates matters, and a complete explanation of the stepped curves requires more knowledge than we have yet obtained on the mechanism of the production of charges at this stage in the life of the cloud.

### *The Nature of the Ions.*

It is seen from fig. 1 that a field of 99 volts on the ionization chamber, whilst collecting the majority of the smaller ions in the cloud, has little appreciable effect upon the large ions. Since this field is sufficient to produce saturation currents for ions of mobility as low as  $1.0 \times 10^{-4}$  cm./sec./volt/cm., the large ions in general must be less mobile than this and the small ions more mobile. The mobility of the slowest moving ions in the cloud at any time can be determined if we know the time  $T$ , required for them to cross the electric field. With the usual notation the mobility

$$k = \frac{1}{2TV}(b^2 - a^2) \log_e \frac{b}{a}, \quad . \quad . \quad . \quad (6)$$

where  $V$  is the voltage applied to the ionization chamber. Since the large ions cannot be detected by the method of stopping or restarting the flow of cloud through the ionization chamber until the cloud is about 20 minutes old, the earlier values of  $T$  must be less than 2 minutes, corresponding to a mobility greater than  $2.8 \times 10^{-5}$ . We have seen that the value  $T$  can be obtained from the rise curves of fig. 3, even if a production of new ions is taking place in the cloud. For these curves an approximate value of  $T$  is good enough to give the order of magnitude of the mobility since the product  $kT$  is a constant. For the two rise curves after the minimum we may take  $T$  as 10 minutes and 20 minutes respectively, which lead to values of  $k$  equal to  $5.6 \times 10^{-6}$  and  $2.8 \times 10^{-6}$ . Since, moreover, we have both small ions and large ions present in the cloud at all times (as is shown by the curves of fig. 1 for the various field strengths), the shape of the rise curves indicates that we must have ions present in the cloud with varying mobilities between those of the small ions and that of the slowest moving ions present. If this were not so and the ions in the cloud were grouped about comparatively few characteristic mobilities, the rise curves would be stepped and not smooth. The times of occurrence of the steps would give these characteristic mobilities.

It therefore appears that in the initial stages of the cloud the ions present are relatively fairly mobile, but as the cloud ages new ions appear with continuously diminishing mobilities and the process continues until the ionization currents become too weak to be measured.

If we knew the shape of the ions it might be possible to determine their size. We can obtain some idea, however, by determining the size of a spherical particle of the same mobility carrying a charge equal to that of the electron, by means of the Stokes-Cunningham equation. The radius  $a$  of the particle is given in terms of the mobility  $k$ , the coefficient of viscosity  $\eta$ , and the mean free path of the gas molecules  $\lambda$ , by

$$a = \frac{e}{6 \pi \eta k} \left( 1 + 817 \frac{\lambda}{a} \right). \quad . \quad . \quad . \quad (7)$$

Taking  $e = 4.77 \times 10^{-10}$ ,  $\lambda = 7.5 \times 10^{-6}$ , and  $\eta = 1.78 \times 10^{-4}$ , its value at  $15^\circ \text{C.}$ ,

$$a = \frac{4.74}{k} \left( 1 + \frac{6.13 \times 10^{-6}}{a} \right) \times 10^{-10} \text{ cm.} \quad . \quad . \quad (8)$$

The value  $k = 4.0 \times 10^{-4}$ , the lower limit to the mobility of the small ions, gives  $a = 3.35 \times 10^{-6} \text{ cm.}$  This then is the upper limit to the size of the ions responsible for the initial rapid fall in the ionization current.

Whytlaw-Gray and Speakman<sup>(8)</sup> from direct counts and microbalance determinations of mass, estimate the average size of the ultramicroscopic particles in the initial stages of similar clouds as spheres of radius  $5.0 \times 10^{-6} \text{ cm.}$  The agreement is sufficiently close to show that the small ions of these clouds are actually charged particles of ultramicroscopic size. Since amicrons seem to be always present initially, in relatively large numbers, a small proportion of amicrons carrying charges will suffice to account for the difference in values obtained by the two methods.

At 20 minutes in the life of the cloud of fig. 3, the large ions have mobilities greater than  $2.8 \times 10^5$  corresponding to a radius  $a = 2.2 \times 10^5 \text{ cm.}$ , and the limiting mobilities from the rise curves  $k = 5.6 \times 10^{-6}$  and  $k = 2.8 \times 10^{-6}$  correspond to particles of radius  $9.11 \times 10^{-5} \text{ cm.}$  and  $1.76 \times 10^{-4} \text{ cm.}$

If we compare the volumes of the ultramicros forming the small ions with the volumes of the particles constituting the large ions, it seems very clear that the large ions must arise by the coagulation of large numbers of ultramicros.

The general decrease of mobilities throughout the life-history of the cloud shows that, so far as the charged particles are concerned, there must be a gradual decrease in the number of particles per unit volume of the cloud due to a process of coagulation. This is in complete agreement with the deductions of Whytlaw-Gray from totally different evidence, and is clearly brought out by the remarkable series of photo-micrographs of deposits from arc clouds which he has published.

### *Summary.*

Types of ionization curves obtained from cadmium oxide clouds produced in dry air free from dust and carbon dioxide by an arc discharge, are described. In the later stages of the cloud the ions present at any time are not of uniform mobility. The average mobility of the ions in the cloud and the mobility of the slowest moving ions present at any time diminish as the cloud ages. The dimensions of the ions and the dimensions of the particles in the clouds are of the same order of magnitude, which indicates that the ions are the charged particles of the cloud. The changes in mobility show that coagulation of the particles occurs as the cloud ages.

Under certain circumstances, the ionization curves after decreasing owing to recombination of ions, subsequently show a rise in current strength and become oscillatory. On the usual assumption that the ionization current is proportional to the ionization in the cloud, this indicates that a production of new charges occurs as the clouds age. The new charges appear mainly on particles of low mobility.

My thanks are due to Professor R. Whytlaw-Gray both for proposing the research and for the interest he took in the progress of the work. To Professor W. L. Bragg I am indebted for much constructive criticism.

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The University, Manchester.

### *References.*

- (1) De Broglie, *C. R.* cxlvi. p. 624 (1908).
- (2) De Broglie, *C. R.* cxlviii. p. 1163 (1909).
- (3) McClelland, *Proc. Camb. Phil. Soc.* x. p. 241 (1900).
- (4) Ehrenhaft, *Sitz. Akad. Wiss. Wien*, cxix. p. 830 (1910).
- (5) Whytlaw-Gray and others, *Proc. Roy. Soc. A.* cii. p. 600 (1923).
- (6) Walmsley, *Phil. Mag.* xxvi. p. 400 (1913).
- (7) Townsend, 'Electricity in Gases,' p. 134 (Oxford 1915).
- (8) Whytlaw-Gray, *loc. cit.* p. 621.

**CXIV. Some Experiments on Hydrogen Over-potential at a Mercury Cathode and a Discussion of their Bearing on Current Theories.** By A. L. McATLAY, F.Inst.P., and F. P. BOWDEN, M.Sc.\*

THE following is an account of some experiments on hydrogen over-potential at a mercury cathode with mixed electrolytes containing metal and hydrogen ions.

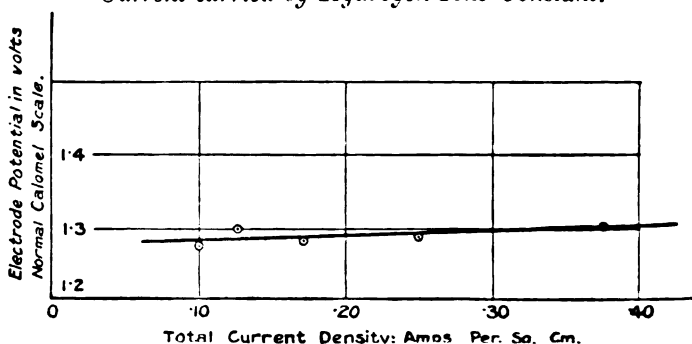
These experiments provide information which is used in a critical discussion of theories of over-potential.

### EXPERIMENTS AND RESULTS.

The experiments were essentially measurements by the direct method of the over-potential at zinc and mercury surfaces using an electrolyte composed of varying proportions of sulphuric acid and zinc or mercury sulphate, together with periodic weighings of the cathode to determine the relative amounts of current carried by metal and hydrogen ions. Their object was to investigate the relations between the over-potential, the total current passing through the cathode surface, and the current conveyed to the surface by hydrogen ions only.

The results of these experiments lead to two general conclusions. First the magnitude of the over-potential is determined only by the current carried by the hydrogen ions and the nature of the cathode, and is almost independent of the total current flowing. The figure shows how nearly

*Electrode Potential against Total Current Density  
Current carried by Hydrogen Ions Constant.*



true this is. Here the single electrode potential at a mercury cathode on the normal calomel scale is plotted against total current density. The electrolyte consisted of a different mixture of sulphuric acid and zinc sulphate for

\* Communicated by the Authors.

each point on the graph. It was so adjusted that the current carried by the hydrogen ions was in every case very nearly 1 amp. per sq. cm. The left-hand point was obtained with pure acid as electrolyte. It will be seen that with an over-potential of about 1.0 volt for a range of total current density of nearly 1 to 4 there was only a variation of about 2 per cent. in the over-potential. With a mercury cathode it is possible to obtain measurements reproducible within a few millivolts. If similar experiments be made with solid cathodes the variations in the nature of the surface give large secondary effects, some irregular, and some, more dangerous, systematic. Effects due to such causes as pitting from corrosion by acid and repair of the surface by plating are large.

The second general conclusion is that when an over-potential film is established metals deposit at a potential characteristic of hydrogen, although before the film forms they may deposit at much lower potentials from the same electrolyte. This is not due to low concentration of metal ions in the neighbourhood of the cathode. Stirring has no effect. The phenomenon may be observed with a mercury salt in solution, in which case a high over-potential appears suddenly with no change in current density or other external conditions\*, and both mercury and hydrogen deposit at a cathode potential 1.5 volts more negative than that at which mercury was being deposited an instant before.

It appears, therefore, that the mercury ions play no primary part, either as constructive or destructive agents, in the production of the over-potential film, but that the film hinders their deposition in such a way that the work required to convey unit charge across the cathode boundary is the same whatever ions convey the charge.

The magnitude of the change in the free energy of the metal on deposition (which is measured by its reversible deposition potential) does not affect the cathode potential when the film is present, although a large part of the current is being carried by the metal ions.

#### DISCUSSION OF THEORIES.

1. *Ohmic Resistance Theory.*—The above experiments are obviously extremely hard to explain on this theory, as they seem to show that the over-potential is actually independent of the current density.

2. *Active Film Theory.*—The experiments can be explained by the presence on the cathode of a layer of an active modification of hydrogen, such as monatomic hydrogen, provided

\* McAulay and Bowden, *Proc. Roy. Soc.* (read Feb. 25, 1926).

that the velocity of evaporation of hydrogen ions is much greater than that of the supply of metal ions. If this is so it will be possible for the hydrogen film of high free energy to maintain its over-potential, and the excess energy forced upon the metal ions will appear as kinetic energy which will be dissipated as heat as the cathode is bombarded. However, the results obtained with a cathode-ray oscillograph by Newbery\* advance an argument against this theory. Newbery's photographs show that the disappearance of the greater part of the over-voltage takes place in an interval small compared with a thousandth of a second, whereas, if the layer of active hydrogen were even one atom thick the time required for its dissipation would be expected to be considerably greater than this.

3. *Desorption Theory*.—A theory similar to that suggested by Rideal† in 1920 appears to fit many of the facts in a satisfactory way. Rideal proposed that over-potential might be due to the work required to desorb hydrogen molecules which were adsorbed to the cathode surface, covering it with a continuous layer, and preventing the deposition of further ions. Evidently the work required to desorb a molecule of adsorbed hydrogen should be independent of the nature of the desorbing ion, and so it would appear natural that both hydrogen and metal would be deposited simultaneously and non-preferentially. The difficulty arising from the fact that the metals investigated were divalent may be explained in more than one way. The following suggests itself as plausible. The abstraction of two electrons from a surface on which an over-potential film is established may necessitate the desorption of two atoms, because metallic conduction does not exist in the film, and the desorbing ion can only detach the electron which attaches the adsorbed atom. A single atom may be desorbed by a hydrogen ion.

This theory evidently indicates that during the adsorption of the hydrogen atoms a current should flow on to the cathode at a potential very much lower than that necessary for bubble formation at atmospheric pressure, for the adsorbed film must have a low free energy. To form a monomolecular layer a quantity of electricity of the order of  $10^{-3}$  coulomb must flow on to the cathode. In experiments with a pure normal acid electrolyte and a current density of about  $10^{-5}$  amp./cm.<sup>2</sup>, it was found that the single electrode potential at a mercury cathode increased with time from potentials of about +.4 on the calomel scale.

An objection to the theory arises from the fact, frequently

\* Newbery, Proc. Roy. Soc. cvii. A (1925).

† Rideal, Journ. Am. Chem. Soc. 1920.

observed by the writers, that when a large current (1 amp. per sq. cm.) is passed through pure normal acid to a mercury cathode an over-voltage of more than .5 volt remains after the circuit is opened. This over-potential decays at different speeds according to circumstances, but some continues to exist for a time of the order of minutes. Some of Newbery's photographs also indicate the existence of this effect.

4. *Slow Transformation of a Product between H and H<sub>2</sub>.*—The effect just discussed, that is the persistence of an over-potential on open circuit, renders it difficult to maintain a theory which ascribes over-potential to a high concentration produced by the slowness of some stage in the transformation of hydrogen ions to hydrogen gas.

The above discussion finds some objections to all the usual theories of over-potential. Many of these objections, however, are not fatal. They seem to be least serious in the case of that which supposes that a film of high free energy is formed and behaves as an electronegative cathode. It may be that this theory, combined with the desorption theory to account for the very rapid first fall of potential on opening circuit, will be thought to be most acceptable. It is intended to carry out further experiments on the lines suggested above, with a view to narrowing further the theoretical possibilities.

#### SUMMARY.

It is shown that the over-voltage at a mercury cathode with a mixed electrolyte containing acid and metallic salt is independent of the total current flowing. It is the same for large ranges of total current if the current carried by the hydrogen ions is the same in each case.

When over-voltage is established, hydrogen and metal are both deposited at a high potential characteristic of hydrogen, whatever the reversible potential of the metal.

Four theories which have been advanced to explain over-potential are discussed in the light of these and other experiments. It is shown that the evidence is strongly against the theory which accounts over-potential the result of an ohmic resistance, and also against that which supposes it to be due to a high concentration produced by the slowness of a stage in the transformation of hydrogen ions to hydrogen gas. It is suggested that a combination of the theory of an active film of hydrogen or hydride, whose high free energy provides part of the over-potential, with the view that a further over-potential is necessary for the desorption of this film might explain all the known facts.

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CXV. *Note on the Second Law of Thermodynamics.*

By W. F. SEDGWICK, M.A.\*

AS is well known, W. Thomson expressed the second law of Thermodynamics, in his paper "On the Dynamical Theory of Heat" (Trans. R. S. Edin. 1851, vol. xx. p. 265; or Math. and Phys. Papers, i. p. 179), in the following terms:—

"It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects."

In his review of the second edition of Tait's 'Sketch of Thermodynamics,' 1877 (Nature, 1878, vol. xvii. p. 279; or Scientific Papers, ii. p. 669), Maxwell took exception to this statement of the law, remarking that—

"Without some further restriction this axiom cannot be considered as true, for by allowing air to expand we may derive mechanical effect from it by cooling it below the temperature of the coldest of surrounding objects."

Maxwell goes on to state that—

"If we make it a condition that the material agency is to be left in the same state at the end of the process as it was at first, and also that the mechanical effect is not to be derived from the pressure of the hot or of the cold body, the axiom will be rendered strictly true, but this brings us back to a simple re-assertion of Carnot's principle, except that it is extended from heat engines to all other kinds of inanimate material agency."

By the statement that with the suggested alteration the axiom merely amounts to a re-assertion of Carnot's principle, Maxwell presumably means that the revised axiom merely lends itself to the completion of the familiar proof of the maximum efficiency of the reversible engine, in which the supposed more efficient irreversible engine drives the reversed reversible engine, drawing the same heat from the source that the reversed engine returns to it; with the result that work would be done at the expense of heat drawn from the refrigerator, contrary to the axiom, which asserts such an operation to be impossible by any "inanimate material agency." Even so it may be remarked that if the axiom, with Maxwell's limitations, is sufficient for the establishment of Carnot's principle, it has served its main purpose.

But with regard to Maxwell's criticism of Thomson's form of the law, it will be observed that in the case which he brings forward as conflicting with that law the work is done at the expense of the intrinsic energy of the expanding and

\* Communicated by the Author.

cooling air (Thomson's "portion of matter"), and that no heat is actually withdrawn from the air to any other of the surrounding objects, *e.g.* to a working heat engine. In fact the air may be said to cool itself in the process of doing work. It seems highly probable, however, that in using the words "by cooling it" Thomson intended them to be taken in the transitive, or active, sense which they naturally bear; and that what he had in mind was the actual withdrawal of heat, in the form of heat, from the "portion of matter" (*e.g.* the refrigerator) by another body (*e.g.* the heat-engine), and its subsequent conversion into mechanical effect by this second, independent body. Taken in this sense, Thomson's form of the second law appears to be true, as an expression of a fact of experience (*cf.* Silvanus Thompson's 'Life of Lord Kelvin,' 1910, p. 284). It formulates a limitation which we should expect to hold good on the theory that differences of temperature are due to differences in the average kinetic energy of translation of the molecules of a body, and that accordingly equality of temperature between two bodies is only attained when the average kinetic energy of translation of the molecules within one of the bodies is in equilibrium with the average kinetic energy of translation of the molecules in the other. For under such conditions, although groups of molecules in one body may from time to time impart heat or energy to groups of molecules in the other body which at the time have less energy of motion, such an effect would not occur on the average, or for any appreciable amount of time, having regard to the enormous, though still finite, number of molecules concerned (*cf.* Maxwell, *l.c.* pp. 670-1). Consequently we should not expect that it would be possible to extract heat from any portion of matter unless there were some body in the neighbourhood at a lower temperature, however small the difference, than the matter in question; if two bodies started at equal temperatures, the transference of heat from one to the other would immediately and necessarily begin to involve the impossible result of a transference of heat from the colder to the hotter.

In Maxwell's expanding and self-cooling air-piston there is no actual transference of heat to any external body, whether cooler or hotter; but the energy of motion of the molecules of the air is merely drawn on to cause the piston to move against an external resistance which is at first, at all events, necessarily smaller, when all the forces are taken into account, than the resultant pressure due to the air in the piston; and there is nothing in the molecular theory in conflict with the supposed motion of the piston.

In order to preclude the construction placed upon it by Maxwell, it is suggested that Lord Kelvin's form of the Second Law of Thermodynamics might be modified so as to run as follows:—

It is impossible, by means of inanimate material agency, to derive mechanical effect through a direct transference of heat, in the form of heat, to another body from any portion of matter which is at or below the temperature of the coldest of the surrounding objects.

In the third edition of Preston's 'Theory of Heat,' as revised by J. R. Cotter, 1919, it is stated (Art. 324, p. 684) that Prof. W. M'F. Orr has devised the following alternative form of Lord Kelvin's axiom, viz. :—

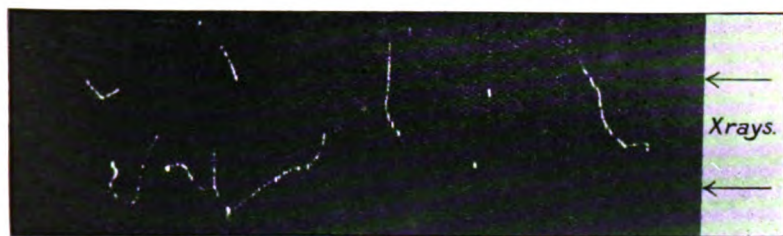
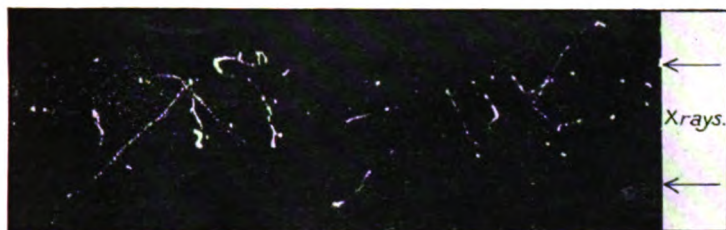
"If a system interchanges heat with external bodies at one assigned temperature only, then it is impossible that in a cycle it should, on the whole, receive heat from external bodies, and (as a necessary consequence by the first law), on the whole, do work on external bodies."

In this form the law would apply to the higher as well as to the lower of the two temperatures in an ordinary cycle; the actual transference of heat at the lower of the two temperatures being annulled, in the complete cycle contemplated in the revised axiom, by the superposition of two opposing cycles, in the customary manner. The axiomatic character of the law when applied to the higher temperature is, however, by no means so obvious as in the case of its application to the lower temperature. Moreover, there appears to be no sufficient reason for the complication of Lord Kelvin's form of the second law by the introduction of the idea of a cycle; provided the axiom is restricted, as suggested above, so as to apply only to operations involving a direct transfer of heat.

On the same page of Preston's book there is also given a revised form of Clausius' expression of the second law, likewise due to Prof. Orr. But Clausius' "rather dubious axiom" (as Tait describes it in § 53 of the first edition of his 'Sketch of Thermodynamics,' 1868), besides being inherently less axiomatic than Lord Kelvin's, also labours under the disadvantage, as compared with the latter, of necessitating the consideration of two temperatures instead of one only, and that the lowest. For these reasons it seems preferable to found the theory on Lord Kelvin's axiom, which connects itself with, and is indeed almost a deduction from, the kinetic theory of heat, in a manner which could not be claimed for its rival form.

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[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

AIR.  $\lambda = 57 \text{ \AA}$ AIR.  $\lambda = 35 \text{ \AA}$ OXYGEN.  $\lambda = 709 \text{ \AA}$ OXYGEN.  $\lambda = 614 \text{ \AA}$ OXYGEN.  $\lambda = 54 \text{ \AA}$



6.



NITROGEN.  $\lambda = 614 \text{ \AA}$ .

7.



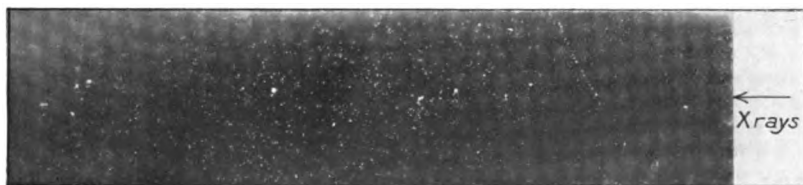
NITROGEN.  $\lambda = 545 \text{ \AA}$ .

8.



ARGON.  $\lambda = 614 \text{ \AA}$ .

9.



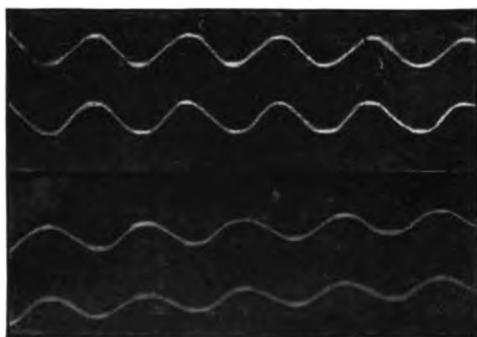
HYDROGEN.  $\lambda = 614 \text{ \AA}$ .

10.



HYDROGEN + 1% ARGON.  $\lambda = 614 \text{ \AA}$ .









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